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SYNTHESES OF NOVEL NITROGEN
AND PHOSPHORUS HETEROCYCLES

Contract No. F49620-82-C-0021

Final Report, SN-2007-F

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CHEMICALS AND MATERIALS RESEARCH DEPARTMENT

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26 April 1985

Ultrasystems, Inc.
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Irvine, California 92714

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Air Force Office of Scientific Research
Directorate of Chemical Sciences
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Perfluoro-n-octanonitrile was found to react with aniline both in the absence and presence of solvents. A spectrum of products was formed including tris(perfluoro-n-heptyl)-s-triazine, N-phenyl-perfluoro-n-octylamidine, and N'-(perfluoro-n-octylimidoyl)-N-phenyl-perfluoro-n-octylamidine, as well as the diphenyl analogues of the last two compounds.

Treatment of perfluoro-n-octanonitrile with phenylphosphine gave tetraphenyltetra-phosphine and a spectrum of reduction and interaction products of perfluorooctanonitrile, as well as phenylphosphine addition compounds. Both linear and cyclic materials were identified. The formation of some of the interaction products was associated with ammonia elimination. Depending on reaction conditions, specific phosphorus-containing compounds could be preferentially produced. All the structure assignments are based solely on mass spectral breakdown patterns, since pure compounds were not isolated.

With diphenylphosphine, perfluoro-n-octanonitrile gave two products: a primary adduct, $C_7F_{15}C(=NH)P(C_6H_5)_2$, and the reduced adduct, $C_7F_{15}CH(NH_2)P(C_6H_5)_2$. Presence of water prevented the formation of the reduced compound; the latter was not produced by reduction of the primary adduct.

FOREWORD

This Final Report describes the work performed
by the Chemicals and Materials Research Department,
Ultrasystems, Inc. under Contract F49620-82-C-0021,
"Syntheses of Novel Nitrogen and Phosphorus Hetero-
cycles". The investigations were carried out during
the period 1 March 1982 to 28 February 1985 by J. H.
Nakahara, D. H. Harris, M. E. Smythe, R. H. Kratzer,
and K. L. Paciorek, Project Manager. This contract
was administered by the Directorate of Chemical
Sciences, Air Force Office of Scientific Research,
with Dr. Anthony J. Matuszko as Technical Program
Manager.

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1. ABSTRACT

1-Dichlorophospha-3,5-perfluoro-n-heptyl (or perfluoro-alkylether)-2,4,6-triazines were synthesized by interaction of imidoylamidines with phosphorus pentachloride. In a parallel approach, 1,3-bis(phenylchlorophospha)-5-perfluoroalkyl (or perfluoroalkylether)-2,4,6-triazines were obtained from the reaction of amidines with imido-diphenyl-diphosphinic acid pentachloride. Replacement of chlorine by thiophenyl and azido groups proceeded readily. Di-(phenylchlorophospha)-s-triazine was found to undergo further reaction with amidine in a 1:2 ratio. The existence of stereo-isomerism was indicated. The thiophenyl-substituted phospha-s-triazines functioned as corrosion and oxidation inhibitors in perfluoroalkylether fluids; however, their thermal and thermal oxidative stability was lower than that of the phenyl analogues. Both the mono- and diphospha-s-triazines were completely degraded in 24 hr at 316°C in nitrogen; diphenylsulfide was one of the major products. Mass spectral analysis of the phenyl-free phospha-s-triazines revealed that the specific breakdown patterns are ring specific not phenyl-substituent dependent.

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2. INTRODUCTION

Under Contracts No. F44620-76-C-0065 and F49620-79-C-0037, novel monomeric and polymeric six- and eight-membered heterocyclics containing carbon, nitrogen, and phosphorus ring atoms were synthesized and their thermal and thermal oxidative stabilities evaluated [1-12]. These materials, in particular the six-membered ring members of the series, exhibited anticorrosion and antioxidative action when used as additives in perfluoroalkylether fluids in the presence of metals or metal alloys.

All the compounds prepared to date were substituted on the ring phosphorus atoms by phenyl groups with the exception of monophospha-s-triazine [1] where the phenyl was replaced by pentafluorophenyl moiety. The latter, however, were found to be thermally unstable [4]. One of the objectives of the current program was to prepare phospha-s-triazine ring systems with substituents other than phenyls on the phosphorus ring atoms. This was to include also fused ring systems. Having functional groups on phosphorus would permit the introduction of different groups onto phosphorus and thus open new avenues to structure property tailoring, as well as provide monomers amenable to homo- and copolymerizations.

No studies of reactions of perfluorinated nitriles with phosphines were reported to date. Yet, in analogy with the materials derived from nitrile-ammonia interactions, the potential for novel systems development appeared very promising. Accordingly, a portion of investigations carried out under the subject contract were directed at synthesis and evaluations of functional phospha-s-triazines and assessment of the phosphine-perfluoroalkylnitrile chemistry.

3. RESULTS AND DISCUSSION

3.1 Attempted synthesis of fused ring systems

Interaction of perfluoroalkyl- and perfluoroalkylether amidines with imido-tetraphenyl-diphosphinic acid trichloride was found to give diphospha-s-triazines [3]. In analogy, it was expected that a condensed ring arrangement will result from the reaction of dichlorophosphazene trimer with an amidine, i.e.:

$$Cl_2P \underset{N}{\overset{N}{=}} \overset{Cl_2}{P} \underset{N}{\overset{N}{=}} PCl_2 \quad + \quad 2R_fC \overset{NH}{\underset{NH_2}{\Big\langle}} \quad \longrightarrow \quad$$
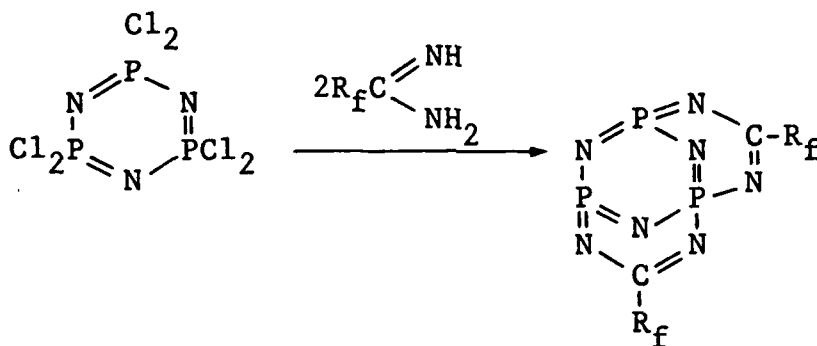
Conducting the reaction at 50°C with perfluoro-n-octanoylamidine resulted in an abstraction of ∿1.5 chlorines per molecule of the amidine based on the produced triethylamine hydrochloride. A mixture of products was obtained which resisted all purification attempts. At 50°C, the corresponding imidoylamidine failed to abstract chlorine from dichlorophosphazene trimer. Raising the temperature to 90°C afforded some triethylamine hydrochloride; however, the imidoylamidine was largely recovered. In view of the known transformation of perfluoroalkyl imidoylamidines to triazines in the vicinity of 100°C, as well as the dissociation of imidoylamidines to amidine and nitrile at these temperatures, it is quite likely that the observed reaction was due to the liberated ammonia and/or amidine. In view of the above, this approach was abandoned.

3.2 Chloro-substituted diphospha-s-triazines and derivatives; syntheses and characterizations

This study was undertaken to evaluate the reactivity of

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had more influence on the fragmentation behavior.

In the breakdown patterns of the di(thiophenyl)monophospha-s-triazines, the fragment B, m/e 289, characteristic of other monophospha-s-triazines synthesized to date, described previously [2] and in the current report, was present only in a low proportion. A related ion,

$$(C_6H_5S)_2P \underset{N - CC_2F_4}{\overset{N^+}{\rlap{=}}} \qquad \text{m/e, 389}$$
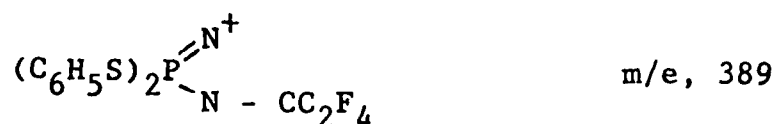
was produced by 1-di(thiophenyl)phospha-3,5-bis(perfluoroalkyl-ether)-2,4,6-triazine (XII). However, the major processes involved the loss of thiophenyl and phenyl disulfide moieties as evidenced by the presence of metastables at m/e 846.3, 789.9, 1008.8, and 951.3 in the mass spectra of Compounds XI and XII, respectively, i.e.,

$$1053^+(M) \longrightarrow 944^+ + 109[SC_6H_5] \qquad m^* \ 846.3$$

$$1053^+(M) \longrightarrow 912^+ + 141[SSC_6H_5] \qquad m^* \ 789.9$$

$$1217^+(M) \longrightarrow 1108^+ + 109[SC_6H_5] \qquad m^* \ 1008.8$$

$$1217^+(M) \longrightarrow 1076^+ + 141[SSC_6H_5] \qquad m^* \ 951.3$$
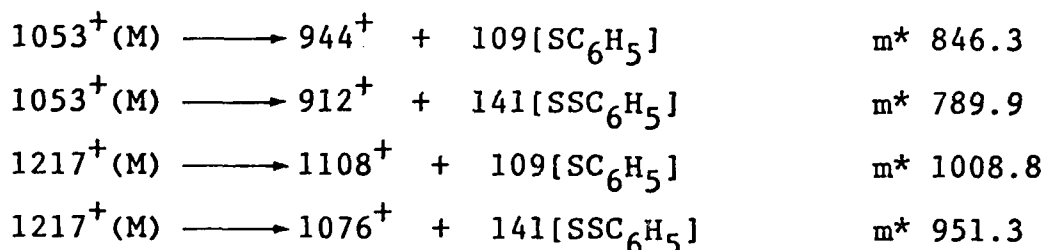
Apparently, the loss of diphenyl disulfide also takes place, as shown by the high intensity peak at m/e 218. The remaining fragment, m/e 835, is of very low intensity, 1% in the case of Compound XI, although it is relatively intense, 9% (999^+), in Compound XII. In both compounds, the thiophenyl moiety, m/e 109, constitutes the 100% peak. As would be expected in the case of 1-di(thiophenyl)phospha-3,5-bis(perfluoro-alkylether)-2,4,6-triazine, fragmentation of the perfluoroalkyl-ether side chain is responsible for a number of the high mass peaks, e.g., m/e 1198, 1051, 932, 866, and 766.

and azido compounds, respectively. In the case of 1-dichloro-phospha-3,5-bis(perfluoroalkylether)-2,4,6-triazine (Compound VIII), although not the base peak, the 141^+ ion corresponding to the fragment B was still a major intensity peak. This proves further that the observed breakdown pattern is not phenyl-substituent dependent, but is characteristic of the ring system itself.

The loss of one of the perfluorinated side chains in all three members of the series proceeds from the molecular ion as shown by the metastables, e.g.,

VIII 1069^+ ⟶ 618^+ + $451[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]$
$$m*, 357.3$$

IX 905^+ ⟶ 536^+ + $369[C_7F_{15}]$ $m*, 317.5$

X 919^+ ⟶ 550^+ + $369[C_7F_{15}]$ $m*, 329.2$
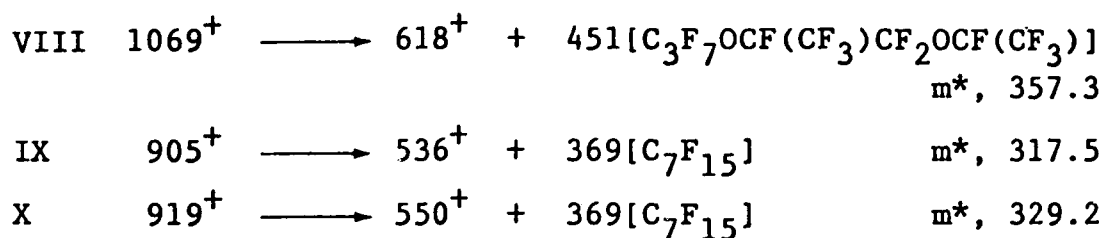
In the case of the perfluoroalkylether-substituted tria-zine (VIII), stepwise fragmentation of the side chains governed by the oxygen presence is supported by the metastables at m/e 657.6 and 330.6, e.g.,

784^+ ⟶ 718^+ + $66[COF_2]$ $m*, 657.6$

618^+ ⟶ 452^+ + $166[CF_3CF_2COF]$ $m*, 330.6$
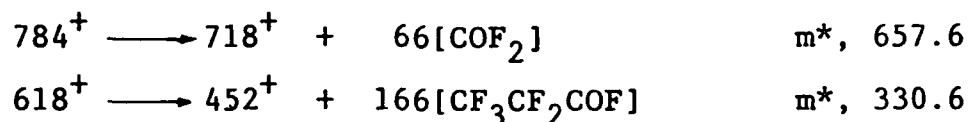
The influence of the oxygen in this compound is also evident from the relatively high abundance of the 241^+ ion which is representative of the β-cleavage.

If one compares the breakdown patterns of the 1-diazido-versus 1-dichloro-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazines, the action of the azido-groups mirrors that of the chloro substituents which was not the case in the diphospha-s-triazine series, discussed in the preceding section. One might have expected two azido groups present on one phosphorus atom, in the absence of the stabilizing action of the phenyl, to have

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Compound IX with perfluoro-n-octanoylamidine in a 1:1 ratio gave a product mix from which no pure substance could be isolated. On the other hand, the diazido-derivative (X) was formed readily by an exchange with lithium azide.

The 1-di(thiophenyl)phospha-3,5-bis(perfluoroalkyl or perfluoroalkylether)-2,4,6-triazines were obtained in good yields by the procedure of Allcock and Kugel [16] that was found effective for the diphospha-s-triazines, i.e.,
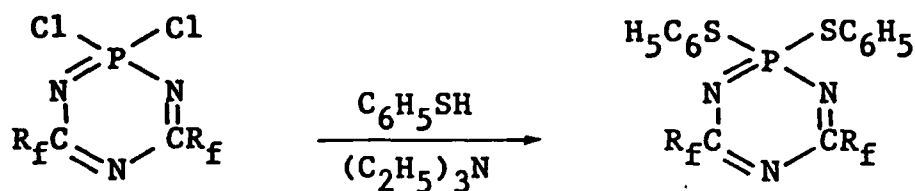
$$\text{XI, } R_f = n\text{-}C_7F_{15}$$
$$\text{XII, } R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$$

The perfluoroheptyl-substituted compounds were solids at room temperature, whereas the perfluoroalkylether-substituted materials were liquids, which is in agreement with what was found in the past [1,7].

The fragmentation patterns of the dichloro- and diazido-monophospha-s-triazines (VIII-X) follow closely those reported for the diphenyl-substituted analogues. The presence of high intensity (>80%) molecular ions in these compounds shows clearly that the stabilizing action of phenyl substituents on the ring is not necessary, which previously was believed to be the case [2]. The characteristic fragment
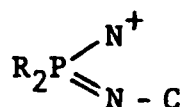
B

constituted the base peak in both of the perfluoro-n-heptyl-substituted materials, peaks at m/e 141 and 155 for the chloro

TABLE 2

Chloromonophospha-s-triazines and derivatives

Compound[a]	Yield %	mp °C	bp °C	IR Bands (cm^{-1})[b]		MW[c]	Elemental Analyses, %						P
							C	H	F	Cl	N	S	
[R$_f$CN]$_2$[Cl$_2$PN] (VIII)	45	-	73-74/0.001 mm Hg	1546(vs),1554(sh)	Calcd	1070.04	20.20	-	60.37	6.63	3.93	-	2.89
					Found	1090.	20.64	-	57.47	6.39	4.32	-	2.82
[n-C$_7$F$_{15}$CN]$_2$[Cl$_2$PN] (IX)	61	30-31	88-89/0.001 mm Hg	1545(vs),1558(sh)	Calcd	906.02	21.21	-	62.91	7.83	4.64	-	3.42
					Found	910.	21.27	-	62.55	7.59	4.79	-	3.41
[n-C$_7$F$_{15}$CN]$_2$[(N$_3$)$_2$PN] (X)	64	35-36	85-90/0.001 mm Hg	2170(vs) (ν,N$_3$) 1550(vs),1555(sh)	Calcd	919.16	20.91	-	62.01	-	13.71	-	3.37
					Found	965.	20.37	-	62.49	-	12.99	-	3.33
[n-C$_7$F$_{15}$CN]$_2$[(SC$_6$H$_5$)$_2$PN] (XI)	71	65.5-67	-	1547(vs),1555(sh)	Calcd	1053.46	31.92	0.96	54.10	-	3.99	6.09	2.94
					Found	1080.	32.19	1.12	52.26	-	3.68	n.d.[d]	3.01
[R$_f$CN]$_2$[(SC$_6$H$_5$)$_2$PN] (XII)	62	-	n.d.	1547(vs),1555(sh)	Calcd	1217.48	29.60	0.83	53.06	-	3.45	5.27	2.54
					Found	1230.	29.29	1.16	50.90	-	3.61	5.29	2.38

a) R$_f$ = C$_3$F$_7$OCF(CF$_3$)CF$_2$OCF(CF$_3$)-.
b) The absorption bands given are characteristic of phosphatriazine ring.
c) Molecular weights determined in C$_6$F$_6$ by vapor pressure osmometry.
d) Not determined.

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its known thermal instability. However, thiophenyl derivatives behave differently from the other compounds.

3.3 Chloro-substituted monophospha-s-triazine and derivatives; syntheses and characterizations

Since diphospha-s-triazines with a chloro group replacing one of the phenyls on each of the ring phosphorus atoms were successfully synthesized, as was discussed in Section 3.2, it was only natural to extend this concept to the monophospha-s-triazines. Douglas and Herring [17] did prepare geminally substituted dichlorotetraphenyl phosphazene trimer via inter-action of imino-bis(aminophosphorane) with phosphorus penta-chloride at elevated temperatures. Based on the similarities of the phospha-s-triazines and phosphazene trimers, one would expect a related approach to lead to dichloromonophospha-s-triazines. These compounds, aside from their potential for introduction of a variety of substituents, were of particular interest with regard to mass spectral breakdown patterns to determine whether the characteristic fragmentations observed to date [2] were really ring-derived or were governed largely by the phenyl substituents on phosphorus.

The novel dichloromonophospha-s-triazines were prepared by the interaction of an imidoylamidine with phosphorus penta-chloride at 0°C in the presence of an acid acceptor.

$$R_fC \underset{\underset{NH}{\|}}{} \underset{N}{\overset{}{}} \overset{NH_2}{\underset{}{}} CR_f \; + \; PCl_5 \longrightarrow R_fC \overset{\overset{Cl_2}{\|}}{\underset{N}{}} P \underset{N}{} CR_f$$
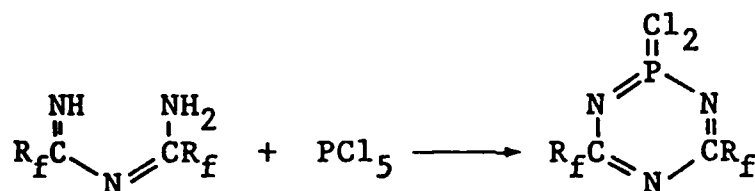
VIII, $R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$

IX, $R_f = n\text{-}C_7F_{15}$

The yields realized of pure Compounds VIII and IX, as evident from the Table 2 listing, are good compared to the phosphazenes [17]. Attempts to prepare a 4-ring compound by reaction of

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$$658^+ \longrightarrow M - 199[(C_6H_5)_2PN]$$

$$230^+ \longrightarrow 429^+ - 199[(C_6H_5)_2PN]$$
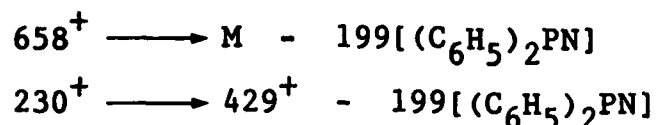
The attendant rearrangement, also observed in the case of the diazido derivative, is further supported by the presence of $(C_6H_5)_2P$ fragment, 185^+ ion, in the mass spectrum.

The fragmentation of the perfluoroalkylether chain is responsible for a number of prominent peaks in the spectrum of 1,3-bis[phenyl(thiophenyl)phospha]-5-perfluoroalkylether-2,4,6-triazine (VII), i.e.,

$$588^+ \longrightarrow M - 351[OCF_2CF(CF_3)OC_3F_7]$$

$$498^+ \longrightarrow M - 109[C_6H_5S] - 332[FOCCF(CF_3)OC_3F_7]$$
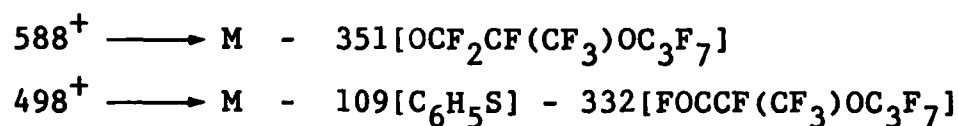
As in the case of the perfluoro-n-heptyl substituted material, the majority of ions involve the loss of the thiophenyl group. This applies to the 498^+, 353^+, and 275^+ ions. The last two ions involve the breakdown of the ring, i.e.,

$$275^+ \longrightarrow M - 109[C_6H_5S] - H - 77[C_6H_5] - R_fCN$$
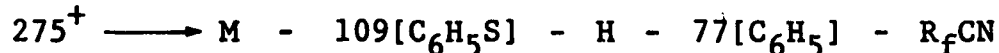
It should be noted that the 353^+ ion formed by the loss of the thiophenyl group and the nitrile moiety is of high intensity in Compound VI, whereas the 275^+ ion is of high intensity in Compound VII. This shows the influence of the perfluorinated chain upon the fragmentation path. In this connection, it is of interest that no loss of $(C_6H_5)_2PN$ fragment is evident in Compound VII indicating that here the loss of phenyl group occurs in preference to the rearrangement.

Based on the infrared and mass spectral data, it is apparent that the ring stability is not significantly affected by replacing a phenyl substituent, in bis(diphenylphospha)triazine, by a chloro, perfluoroalkylamino, or an azido group, although the latter *seems to promote rearrangement in agreement with*

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$(C_6H_5)_2P{\Large{\overset{N^+}{\underset{N=C}{<}}}}$; $(C_6H_5)_2P{\Large{\overset{N}{\underset{}{\diagdown}}}}N^+$; $(C_6H_5)_2P{\equiv}N^+$; $(C_6H_5)_2P^+$

225^+ (16.5%) ; 213^+ (31.8%); 199^+ (16.1%); 185^+ (24.1%)
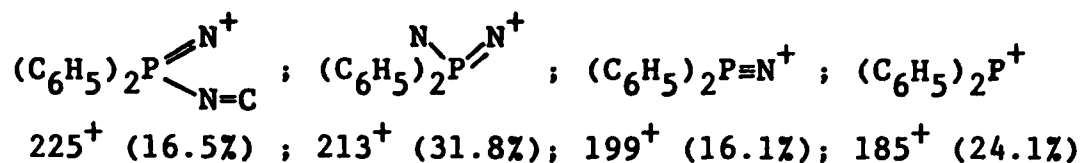
It is noteworthy that the 225^+ ion is characteristic of the diphenylmonophospha-s-triazine series [2].

The mass spectral fragmentation patterns of the thiophenyl substituted materials differ greatly from those of their phenyl, chloro, or even azido and amidino analogues. In the diphospha-s-triazines, the 100% peak, with the exception of the diazido derivative, was formed by the loss of the perfluoroalkyl or perfluoroalkylether moiety. In the thiophenyl-group containing materials, the corresponding ion, m/e 488, amounts to 2%, whereas the loss of the thiophenyl-substituent is the predominant process. The presence of metastables at m/e 652.9 and 733.7 for Compounds VI and VII, respectively, shows clearly that the m/e 748 and 830 ions are formed from the molecular ion, i.e.,

$$857^+(M) \longrightarrow 748^+ + 109[SC_6H_5] \qquad m^* \ 652.9$$

$$939^+(M) \longrightarrow 830^+ + 109[SC_6H_5] \qquad m^* \ 733.7$$
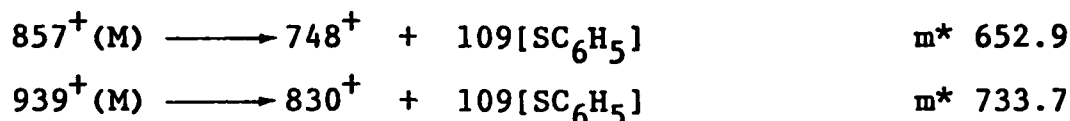
No metastables were observed for the subsequent breakdown of the 748^+ and 830^+ ions. Yet, the most prominent peaks in the spectra involve the loss of the thiophenyl group. This is illustrated for 1,3-bis[phenyl(thiophenyl)phospha]-5-perfluoro-n-heptyl-2,4,6-triazine (VI) by the 429^+, 353^+, and 270^+ ions, i.e.,

$$429^+ \longrightarrow M - 109[C_6H_5S] - 319[C_6F_{13}]$$

$$353^+ \longrightarrow M - 109[C_6H_5S] - R_fCN$$

$$270^+ \longrightarrow M - (2)109[C_6H_5S] - 369[C_7F_{15}]$$
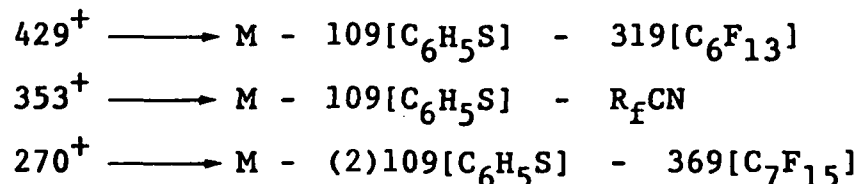
In this particular compound, the loss of the $(C_6H_5)_2PN$ unit, m/e 199, seems to occur to a significant degree as apparent from the 658^+ and 230^+ ions, i.e.,

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In all the compounds discussed above, including the bis(diphenylphospha)- series, the ion corresponding to the loss of the perfluoroalkyl or perfluoroalkylether group was the most intense peak. This, however, is not true for 1,3-bis(phenylazidophospha)-5-perfluoro-n-heptyl-2,4,6-triazine where the base peak corresponds to a loss of an azido group. This ion, 681^+, is formed from the molecular ion as shown by the metastable at 641.4, i.e.,

$$723^+ \longrightarrow 681^+ + 42[N_3] \qquad\qquad m^* \; 641.4$$
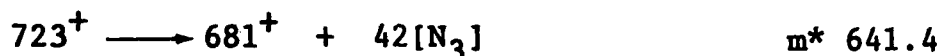
Further breakdown of the 681^+ ion leads to the formation of the 653^+ and 608^+ ions shown by the presence of metastables at m/e 626.2 and m/e 542.8, respectively, corresponding to the processes delineated below.

$$681^+ \longrightarrow 653^+ + 28[N_2] \qquad\qquad m^* \; 626.2$$
$$681^+ \longrightarrow 608^+ + 73[N_3 + P] \qquad\qquad m^* \; 542.8$$
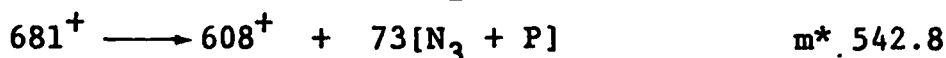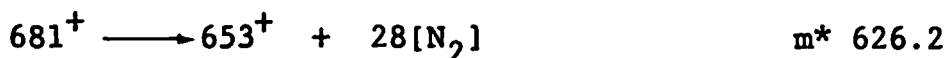
This breakdown is unusual for the diphospha-s-triazine system since it must involve a rearrangement followed by ring breakdown. In all the other members of this series, the loss of a perfluorinated group from the ring carbon atom constituted the major cleavage. The ion corresponding to this fragmentation is present also here, m/e 354^+, however, at a relatively low abundance, 34%. One is tempted to speculate that in the ion 608^+ both of the phenyl groups are situated on the remaining phosphorus atom, i.e.,

$$C_7F_{15}C \underset{N=P}{\overset{N}{<}} \cdots$$

608$^+$
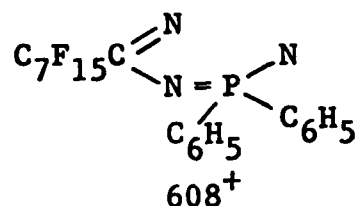
The validity of this postulation is based on the presence in the mass spectrum of several prominent ions which most likely do have this arrangement, e.g.,

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affect the ring stability to electron impact. Strong meta-
stables at m/e 640.7 and 271.8 show that the two processes
depicted below are responsible for the 674^+ and 304^+ ions in
1,3-bis(phenylchlorophospha)-5-perfluoro-n-heptyl-2,4,6-
triazine (II).

$$709^+ \text{ (M)} \longrightarrow 674^+ + 35[Cl] \qquad\qquad m^*\ 640.7$$

$$340^+ \longrightarrow 304^+ + 36[HCl] \qquad\qquad m^*\ 271.8$$
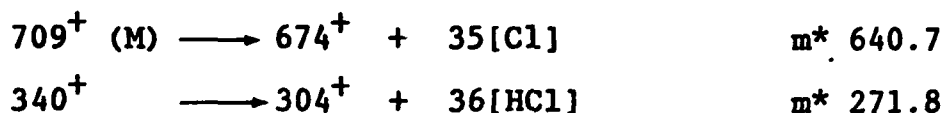
Only the second process was found to take place in the
perfluoroalkylether analogue, Compound I, as evidenced by
the metastable at m/e 271.8.

In the amidino derivative, Compound III, due to instru-
ment limitation, no molecular ion was recorded. The ion
1092^+ corresponds to the fragment A; however, it can also
arise by the loss of the C_7F_{15} group from the amidine side
chain. The 1092^+ ion can lose both the whole amidine side
chain together with an extra hydrogen atom, as shown by the
metastable at 423.4, i.e.,

$$1092^+ \longrightarrow 680^+ + 412[C_7F_{15}C(=NH)NH_2] \quad m^*\ 423.4$$
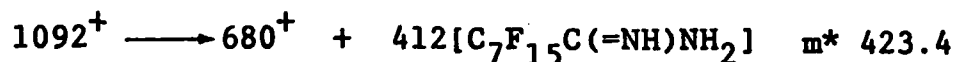
as well as only the amidine function, $C(NH)_2$. The latter
path is confirmed by the presence of the metastable at m/e
1009.6, i.e.,

$$1092^+ \longrightarrow 1050^+ + 42[C(NH)_2] \qquad m^*\ 1009.6$$
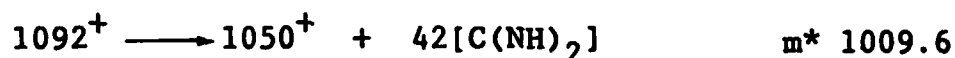
The first process points to Structure A for the 1092^+ ion,
whereas the second breakdown proves initial loss of C_7F_{15}
from the amidine side chain followed by subsequent scission
next to the phosphorus atom. This would imply that both
arrangements are responsible for the 1092^+ ion. The high
intensity ion at 974 originates most likely from the subsequent
loss of a phenyl group and the amidine side chain (minus
hydrogen). The presence of the doubly charged parent ion
730.5^{++} has not been encountered to date in the diphospha-s-
triazines, although the octatetraenes have been found to
produce this type of an ion [6].

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doubt that isomerization did take place. The melting point of what appears to be the thermodynamically more stable isomer is higher than that of the initially formed material which had a melting point of 89-91°C. The existence of cis-trans isomerism in diphospha-s-triazines having two different substituents on the phosphorus atoms is to be expected in analogy with phosphazene chemistry [13]. As noted above, two isomers were also found in the case of 1,3-bis[phenyl(perfluoro-n-octanoylamidino)phospha]-5-perfluoro-n-heptyl-2,4,6-triazine. What is surprising is the absence of the isomerism in the chloro-precursors. On the other hand, it can be argued that the method of synthesis leads to one isomer only.

The mass spectral breakdown patterns of the diphospha-s-triazines, wherein one of the phenyls on each of the ring phosphorus atoms has been replaced by another group, follow closely those reported for the bis(diphenylphospha)-analogues [3]. Thus, in each instance, when not prevented by instrument limitation, molecular ions were observed. For both of the dichloro members of the series, Compounds I and II, the fragment A

A
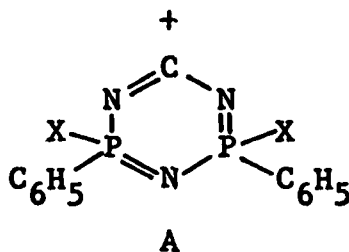
(m/e = 340; X = Cl) was found to constitute the 100% peak. A very weak metastable at m/e 163 for the perfluoro-n-heptyl-substituted material indicates that this ion is formed at least in part from the molecular ion:

$$709^+ \text{ (M)} \longrightarrow 340^+ + 369[C_7F_{15}] \qquad m^* \text{ } 163$$
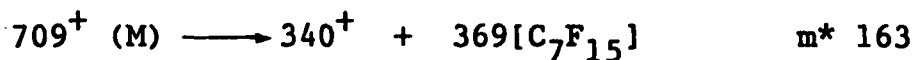
The relatively high intensity of the molecular ions 709^+ and 791^+ for Compounds I and II, respectively, shows that the replacement of two of the phenyl groups by chlorines did not

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The diazido derivative was surprisingly thermally stable to permit its distillation above 150°C.

Interaction of the diphospha-s-triazines with thiophenol following the procedure of Allcock and Kugel [16] gave the desired products in good yields as evident from the data summarized in Table 1, i.e.,
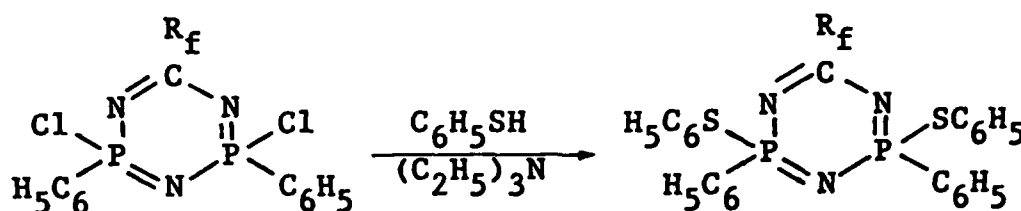
VI, R_f = n-C_7F_{15}

VII, R_f = $C_3F_7OCF(CF_3)CF_2OCF(CF_3)$

The formation of the thiophenyl derivatives was invariably associated with production of diphenyl disulfide, which had to be removed by sublimation and/or extraction. It should be noted that, aside from the *formation of diphenyl disulfide*, the reaction proceeded very cleanly. The purity of all the materials was verified by gas chromatography. 1,3-Bis[phenyl-(thiophenyl)phospha]-5-perfluoroalkylether-2,4,6-triazine (VII) was found to have two peaks in 3:1 ratio (retention times 38.5, 39.5 min) of the same mass spectral patterns pointing to the presence of isomers. The relative ratio of the isomers was not changed by distillation, i.e., residence at elevated temperature. The corresponding perfluoro-n-heptyl substituted analogue (VI) consisted of one isomer only. However, exposure to 235°C resulted in the transformation of ∿75% of the material into another isomer as determined by gas chromatography (retention times 43.4 and 44.8 min). Crystallization from hexane gave the "new" isomer, mp 104-109°C, admixed with ∿10% of the initial material. The mass spectral breakdown pattern and the molecular weight (Calcd. 857.58; Found 900) prove beyond

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melting material on treatment with hot benzene. Whether the two isomers can be represented by the arrangements IIIa and IIIb, or whether one is dealing with cis-trans isomerism which was found to occur in the cyclic phosphazenes [13,14] has not been determined.

$$HN=\overset{\overset{\displaystyle F_{15}C_7}{|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}\diagdown\underset{\underset{\displaystyle C_6H_5}{}}{P}\diagup\overset{\overset{\displaystyle C_7F_{15}}{\overset{|}{C}}}{\underset{\displaystyle N=\diagdown}{N}}\diagdown\underset{\underset{\displaystyle N}{}}{\overset{\overset{\displaystyle N}{||}}{P}}\diagup\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle C_7F_{15}}{|}}{C}=NH$$
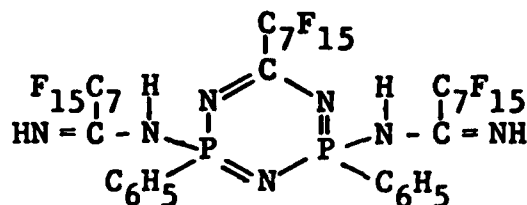
IIIa
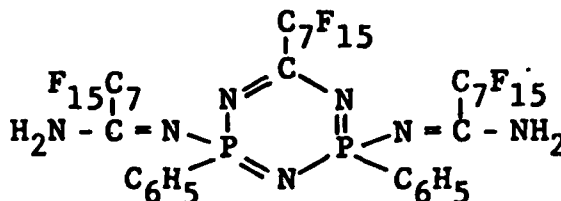
IIIb

When the reaction was carried out using a 1:1 phospha-s-triazine to amidine mole ratio, no bridged or singly-substituted product was isolated. The only compounds identified by gas chromatography were 1,3-bis(phenylchlorophospha)-5-perfluoro-n-heptyl-2,4,6-triazine and the di-amidino derivative.
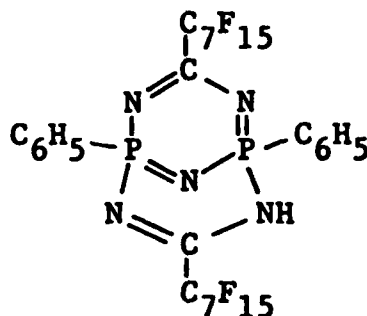
Replacement of the chlorines in the diphospha-s-triazine, Compound II, by azido-groups proceeded readily which was also found to be the case in the corresponding cyclic phosphazenes [15]. 1,3-Bis(phenylazidophospha)-5-perfluoro-n-heptyl-2,4,6-triazine was further characterized by the preparation of the triphenylphosphine derivative, Compound V.

V

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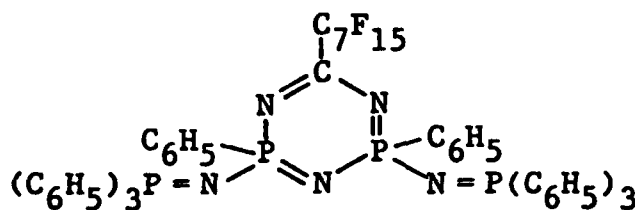
TABLE 1

Chlorophenyldiphospha-s-triazines and derivatives

Compound[a]	Yield %	mp °C	bp °C	IR Bands (cm⁻¹)[b]		MW[c]	Elemental Analyses, %						
							C	H	F	Cl	N	S	P
$[R_fCN][C_6H_5(Cl)PN]_2$ (I)	60	-	130-135/0.001 mm Hg	1494(vs),1501(sh)	Calcd	792.16	31.84	1.27	40.77	8.95	5.30	-	7.82
					Found	810.	31.90	1.51	41.06	8.72	5.21	-	7.83
$[n\text{-}C_7F_{15}CN][C_6H_5(Cl)PN]_2$ (II)	79	59-62	153-162/0.001 mm Hg	1490(vs),1508(sh)	Calcd	710.15	33.83	1.42	40.13	9.99	5.92	-	8.72
					Found	750.	33.84	1.66	39.89	9.70	5.93	-	8.74
$[n\text{-}C_7F_{15}CN][C_6H_5(Am)PN]_2$[d] (III)	72	54-56 103-106	-	1510(vs) 1500(vs),1505(sh)	Calcd	1461.43	29.59	0.97	58.50	-	6.71	-	4.24
					Found	1490.	29.68	1.18	57.90	-	6.62	-	4.24
$[n\text{-}C_7F_{15}CN][C_6H_5(N_3)PN]_2$ (IV)	71	-	148-150/0.001 mm Hg	2140(vs) (ν,N₃) 1497(vs),1503(sh)	Calcd	723.28	33.21	1.39	39.40	-	17.43	-	8.56
					Found	760.	33.32	1.61	40.07	-	17.02	-	8.56
$[n\text{-}C_7F_{15}CN][C_6H_5(N=P(C_6H_5)_3)PN]_2$ (V)	71	59-65	-	1514(vs)	Calcd	1191.84	56.44	3.38	23.91	-	5.88	-	10.40
					Found	1210.	56.57	3.61	22.83	-	5.72	-	9.74
$[n\text{-}C_7F_{15}CN][C_6H_5(SC_6H_5)PN]_2$ (VI)	71	89-91 104-109	-	1495(vs),1502(sh)	Calcd	857.58	44.82	2.35	33.23	-	4.90	7.48	7.22
					Found	880.	44.70	2.37	33.98	-	4.96	7.68	7.21
$[R_fCN][C_6H_5(SC_6H_5)PN]_2$ (VII)	92	-	189/0.001 mm Hg	1495(vs),1502(sh)	Calcd	939.59	42.18	2.15	34.37	-	4.47	6.83	6.60
					Found	950.	42.35	2.33	34.65	-	4.47	n.d.[e]	6.17

a) $R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)-$.
b) The absorption bands given are characteristic of phosphatriazine ring.
c) Molecular weights determined in C_6F_6 by vapor pressure osmometry.
d) $Am = -N=C(NH_2)C_7F_{15}$.
e) Not determined.

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chlorines located on phosphorus in phospha-s-triazines and to
determine the feasibility of preparing differently substituted
ring compounds with the ultimate aim of developing compositions
tailored for specific applications. In 1,3-bis(phenylchloro-
phospha)-s-triazines, the two chlorines are situated on two
different ring phosphorus atoms. The presence of a phenyl
group on the same phosphorus would be thus expected to provide
thermal stability, whereas the "meta" arrangement of the func-
tional groups in a potential polymer derived from this type
of a precursor should impart low Tg characteristics.

1,3-Bis(phenylchlorophospha)-s-triazines were obtained
by interaction of amidines with imido-diphenyl-diphosphinic
acid pentachloride, i.e.:

$$C_6H_5\overset{Cl_3}{P}-N=\overset{Cl_2}{P}C_6H_5 \ + \ R_fC\begin{smallmatrix}\nearrow NH \\ \searrow NH_2\end{smallmatrix} \longrightarrow (C_6H_5)ClP\underset{N}{\overset{N=C(R_f)-N}{\diagdown\diagup}}PCl(C_6H_5)$$
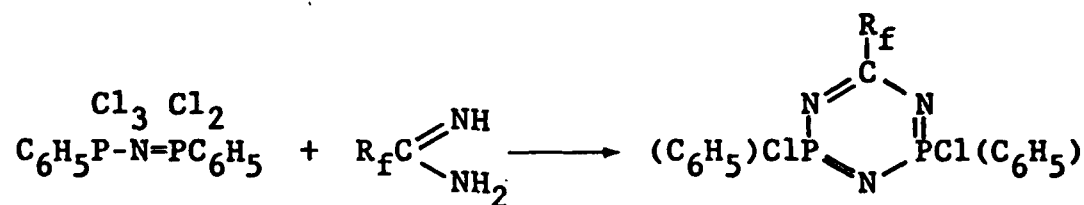
I, $R_f = C_3F_7OCF(CF_3)CF_2OCF(CF_3)$

II, $R_f = n\text{-}C_7F_{15}$

The compounds synthesized are listed in Table 1. The lower
yield of the perfluoroalkylether-substituted analogue, as
compared to the perfluoro-n-heptyl group containing material,
is due to the unavoidable presence of imidoylamidine in the
amidine [3] resulting in the formation of octatetraene [6]
which was separated by distillation. Inasmuch as pure
1,3-bis(phenylchlorophospha)-5-perfluoro-n-heptyl-2,4,6-
triazine was obtained in high yield (79%), it is obvious that
the two chlorines on the ring phosphorus atoms are relatively
unreactive towards the amidine. Yet, in the presence of an
excess of amidine, the substitution of the two chlorines took
place on a one-to-one basis; two isomers were obtained, one
melting at 54-56°C and the other at 103-106°C. The
lower melting compound could be transformed into the higher

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Based on the mass spectra of the thiophenyl group-containing phospha-s-triazines, these compounds would be expected to liberate diphenyl disulfide on thermal degradation.

3.4 Thermal and oxidative stabilities of thiophenyl-substituted mono- and diphospha-s-triazines

To obtain a meaningful comparison of the thermal and thermal oxidative stabilities of the mono- versus diphospha-s-triazines, substituted by thiophenyl groups, investigations were performed on 1-phenyl(thiophenyl)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine (prepared under another program sponsored by the U.S. Air Force [18]) and 1,3-bis[phenyl(thiophenyl)-phospha]-5-perfluoro-n-heptyl-2,4,6-triazine. It is evident from the data listed in Table 3 that the diphospha-s-triazine is definitely more thermally and oxidatively stable, at least at 235°C in air, than the monophospha-s-triazine. Essentially no difference in stability was observed between the corresponding phenyl-substituted mono- and diphospha-s-triazines [4]. The production of diphenyl disulfide is in agreement with the predictions based on mass spectral breakdown patterns, discussed in the preceding section.

The destabilizing effect of the thiophenyl, as compared to the phenyl group, is obvious from the complete decomposition of the thiophenylphospha-s-triazines at 316°C. Under parallel conditions, >90% of the diphenylphospha analogue was recovered unchanged [4]. The four products identified and quantitated were perfluoro-n-octanonitrile, perfluoro-n-heptyl-s-triazine, diphenyl disulfide, and diphenyl sulfide. The thermal trimerization of perfluoroalkyl nitriles is well established [19]. Exposure of diphenyl disulfide in nitrogen to 316°C for 24 hr resulted in 30% recovery of the starting material and 70% transformation into diphenyl sulfide. It can be thus deduced that the triazine and diphenyl sulfide are derived from the primary products, namely perfluoro-n-octanonitrile and diphenyl disul-

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TABLE 3

Degradation studies[a]

Test No.	Compound	Temp °C	Atmosphere	Starting Material Used mg	Starting Material Recovered %	Oxygen consumed mg	Oxygen consumed %[c]	Products (%)[b] $C_7F_{15}CN$	Products (%)[b] $[C_7F_{15}CN]_3$	Products (%)[b] $\Phi SS\Phi$	Products (%)[b] $\Phi S\Phi$
10	$[n\text{-}C_7F_{15}CN][\Phi(\Phi S)PN]_2$	235	Air	926.0	96	2.59	39.5	1.1	0	3.0	-
11	$[n\text{-}C_7F_{15}CN]_2[\Phi(\Phi S)PN]$	235	Air	560.4	67	3.36	41.2	9.0	2.3	6.3	0.8
13	$[n\text{-}C_7F_{15}CN][\Phi(\Phi S)PN]_2$	316	N_2	992.0	0	n.a.[d]	n.a.	24.9	0.2	2.2	16.0
12	$[n\text{-}C_7F_{15}CN]_2[\Phi(\Phi S)PN]$	316	N_2	950.7	0	n.a.	n.a.	40.4	2.6	0.7	6.1

a) The degradations were performed in sealed pyrex ampoules of ca 50 ml volume over a period of 24 hr.
b) Weight percent of starting material.
c) Percent of oxygen available.
d) Not applicable.

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fide. On the other hand, it is plausible that at these elevated temperatures diphenyl sulfide is produced directly from thiophenyl radicals. One would expect the latter to be the initial products of degradation based on the mass spectral evidence. Calculations reveal that during the 24 hr exposure at 316°C, 1,3-bis[phenyl(thiophenyl)phospha]-5-perfluoro-n-heptyl-2,4,6-triazine liberated 82% of the potentially available thiophenyl moieties and 54% of the nitrile, whereas in the case of 1-phenyl(thiophenyl)phospha-3,5-bis(perfluoro-n-heptyl)-2,4,6-triazine, the corresponding values were 77 and 56%, respectively. The fate of the rest of the sulfur and the remainder of the perfluoroalkyl groups is unknown. These, together with phosphorus, comprised the insoluble charred residue.

3.5 Antioxidative and anticorrosive action of thiophenyl-substituted mono- and diphospha-s-triazine

The thiophenyl-substituted mono- and diphospha-s-triazines were evaluated as potential anticorrosion and antioxidation additives for perfluoroalkylether fluids, namely poly(hexafluoropropene oxide) (Krytox 143AC, product of DuPont) and the unbranched fluid, $CF_3O(CF_2O)_x(CF_2CF_2O)_yCF_3$ (Fomblin Z, product of Montedison). Inasmuch as Ti(4Al,4Mn) alloy was found to be significantly more effective in catalyzing the degradation of perfluoroalkylether fluids [20,21,22] than M-50 which was previously used for these tests, it has been employed exclusively in the current investigations.

The results of these tests are summarized in Table 4; for comparison purposes, corresponding tests involving 1-diphenylphospha-3,5-bis(perfluoroalkylether)-2,4,6-triazine were also included. Based on the degradation products formed in the first 24 hr, Tests 1A and 2A, the sulfur-compounds would appear to be effective in arresting degradation. Yet, the exposure was accompanied by the formation of a brown, very fine precipitate. This could be removed by filtration and

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TABLE 4

Effect of phenyl(thiophenyl)phospha-s-triazines on thermal oxidative degradation of perfluoroalkylether fluids in the presence of Ti(4Al,4Mn) alloy[a]

Test No.[b]	Fluid Type	Fluid g	%[c]	Additive Type	Temp °C	Exposure time hr	O_2 Consumed Total mg	O_2 Consumed %[d]	O_2 Consumed mg/g[e]	Total Products Formed mg	Total Products Formed mg/g[f]
62	Krytox 143AC	4.79	-	none	316	24	74.9	68.1	15.7	758.7	158.4
1A	Krytox 143AC	4.78	1.0	$[(\phi S)_2 PN][R_f CN]_2$[g]	316	24	7.9	7.0	1.7	7.7	1.6
1B	Krytox 143AC	3.70	1.0	$[(\phi S)_2 PN][R_f CN]_2$	316	24	12.8	11.4	3.5	126.0	34.0
2A	Krytox 143AC	4.89	1.0	$[(\phi S)\phi PN]_2[R_f CN]$	316	24	2.1	1.9	0.4	8.5	1.7
2B	Krytox 143AC	4.52	0.5	$[(\phi S)\phi PN]_2[R_f CN]$	316	24	2.0	1.8	0.4	22.4	5.0
3A	Krytox 143AC	5.38	1.0	$[\phi_2 PN][R_f CN]_2$	316	24	0.4	0.3	0.1	4.1	0.8
3B	Krytox 143AC	5.38	1.0	$[\phi_2 PN][R_f CN]_2$	316	24	0.0	0.0	0.0	3.9	0.7
5A	Krytox 143AC	3.46	1.0	$[(\phi S)\phi PN]_2[R_f CN]$	316	1	n.d.[h]	n.d.	n.d.	n.d.	n.d.
5B	Krytox 143AC	2.64	1.0	$[(\phi S)\phi PN]_2[R_f CN]$	316	24	6.5	5.8	2.5	71.7	27.2
6A	Krytox 143AC	3.36	1.0	$[(\phi S)\phi PN]_2[C_7 F_{15} CN]$	316	2.2	n.d.	n.d.	n.d.	n.d.	n.d.
6B	Krytox 143AC	3.44	0.6	$[(\phi S)\phi PN]_2[C_7 F_{15} CN]$	316	24	18.3	16.2	5.3	141.3	41.1
7A	Krytox 143AC	3.96	1.0	$[(\phi S)\phi PN]_2[R_f CN]$	316	4	n.d.	n.d.	n.d.	n.d.	n.d.
7B	Krytox 143AC	4.03	0.7	$[(\phi S)\phi PN]_2[R_f CN]$	316	24	4.2	6.0	1.0	68.5	17.1
41	Fomblin Z	3.84	-	none	288	8	51.1	17.2	13.3	2235	582
61	Fomblin Z	2.82	1.0	$[\phi_2 PN][R_f CN]_2$	288	24	0.9	0.8	0.4	2.4	0.9
8A	Fomblin Z	6.10	2.0	$[(\phi S)\phi PN]_2[R_f CN]$	288	8	2.7	2.6	0.4	8.4	1.2
8B	Fomblin Z	5.13	2.0	$[(\phi S)\phi PN]_2[R_f CN]$	288	8	0.8	0.8	0.2	6.8	1.3
8C	Fomblin Z	3.13	2.0	$[(\phi S)\phi PN]_2[R_f CN]$	288	8	n.d.	n.d.	n.d.	6.7	2.1

a) The apparatus consisted of a sealed glass tube wherein the metal coupon was suspended in the fluid; the test was conducted in pure oxygen; at the conclusion of the test, the oxygen was measured and the products were collected and measured.
b) In the A series of tests, untreated fluid admixed with the additive was utilized; in the B and C tests, the filtered residue from the preceding test was utilized. In test 3 no filtration was employed. In tests 2B, 6B, and 7B some fluid was replenished thus lowering the actual additive concentration.
c) The percent is weight percent of additive per weight of fluid used.
d) Percent of oxygen available.
e) Oxygen consumed in mg/g fluid employed.
f) Products formed in mg/g fluid employed.
g) The R_f corresponds to $C_3 F_7 OCF(CF_3)CF_2 OCF(CF_3)$.
h) Not determined.

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the clear solution, on re-exposure to oxygen and alloy at 316°C, did not form additional precipitate, whereas the quantity of products liberated was still significantly lower than in the absence of the additive. In Tests 5A, 6A, and 7A, the fluid was exposed to oxygen and metal coupon at elevated temperature for a short period of time, cooled, and filtered in an inert atmosphere. The filtrate was then re-exposed to the elevated temperature, oxygen, and a new coupon for 24 hr. It was hoped that the pretreatment will prevent the precipitate formation on further heating. Unfortunately, this was not the case. Based on the degradation data, discussed previously, one would not expect 1,3-bis[phenyl(thiophenyl)phospha]-5-perfluoroalkyl-ether-2,4,6-triazine to exhibit any effectiveness as a corrosion and oxidation inhibitor at 316°C, due to its thermal instability at these temperatures. The results obtained indicate that the phospha-s-triazine degradation products, most likely the phosphorus-containing portion, are the active ingredients and that these can continue to function at elevated temperatures.

At the lower temperature, 288°C, in Fomblin Z, the thio-phenyldiphospha-s-triazine was found to arrest drastically the fluid's degradation as compared to the parallel experiment conducted in its absence (see Tests No. 8A, B, C, and 41). The action lasted for at least 24 hr. It should be noted that no precipitate was observed in the fluid after Test No. 8C; furthermore, the products formed consisted essentially of the perfluoroalkylether nitrile. Based on these results, the thio-phenyldiphospha-s-triazines can be considered as useful addi-tives for Fomblin Z fluids, inasmuch as at 316°C the effective-ness of the diphenyl analogues is also, at best, marginal [20].

3.6 Reactions of perfluoro-n-octanonitrile with aniline

Early work by Grivas and Taurins [23,24] has shown that aniline and trifluoroacetonitrile react readily at room temp-erature in polar solvents; however, as reported by these authors

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and others [25], no reaction was found to occur in the absence of solvent. The only product mentioned was the amidine. No reports in the literature could be found regarding the formation of imidoylamidines from the amidines on further reaction with nitriles.

Interaction of perfluoro-n-octanonitrile with aniline in the absence of solvent at relatively high temperatures, 120-140°C, using a 2:1 perfluoro-n-octanonitrile to aniline ratio, gave the amidine, $C_7F_{15}C(NHC_6H_5)=NH$, in $\sim$77% yield, based on the recovered aniline. The major product was tris(perfluoro-n-heptyl)-s-triazine; its formation from the nitrile is catalyzed by ammonia [26,27] which was most likely produced by the reaction of the N-phenyl-perfluoro-n-octyl-amidine with aniline, i.e.:

$$
\underset{\text{XIII}}{C_7F_{15}\overset{\overset{\displaystyle NH}{\|}}{C}\text{-}NH\Phi} \;+\; NH_2\Phi \;\longrightarrow\; \underset{\text{XIV}}{C_7F_{15}\overset{\overset{\displaystyle NH\Phi}{|}}{C}\text{=}N\Phi} \;+\; NH_3
$$
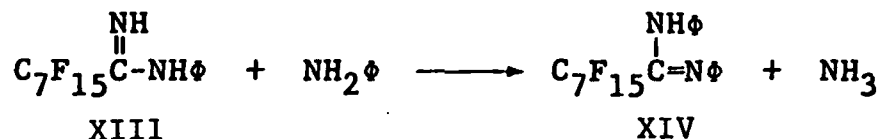
The presence of the interaction product XIV was shown by combined gas chromatography and mass spectrometry (GC/MS). Grivas and Taurins [23,24] have shown the N-aryltrifluoroacetamidines to exist in the imino form XIII shown above; however, for the aniline interaction to take place, the presence of the tautomeric form, i.e.,

$$
C_7F_{15}\overset{\overset{\displaystyle NH}{\|}}{C}\text{-}NH\Phi \;\rightleftharpoons\; C_7F_{15}\overset{\overset{\displaystyle N\Phi}{\|}}{C}\text{-}NH_2
$$
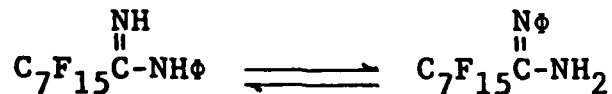
is mandatory. Infrared spectra of the amidine, XIII, and imidoyl-amidine, XV, are given in Figures 1 and 2, respectively.

Pure N-phenyl-perfluoro-n-octylamidine was obtained in 26% yield by reacting aniline and the nitrile in acetonitrile/Freon-113 solvent mixture. Interaction of aniline and perfluoro-

24
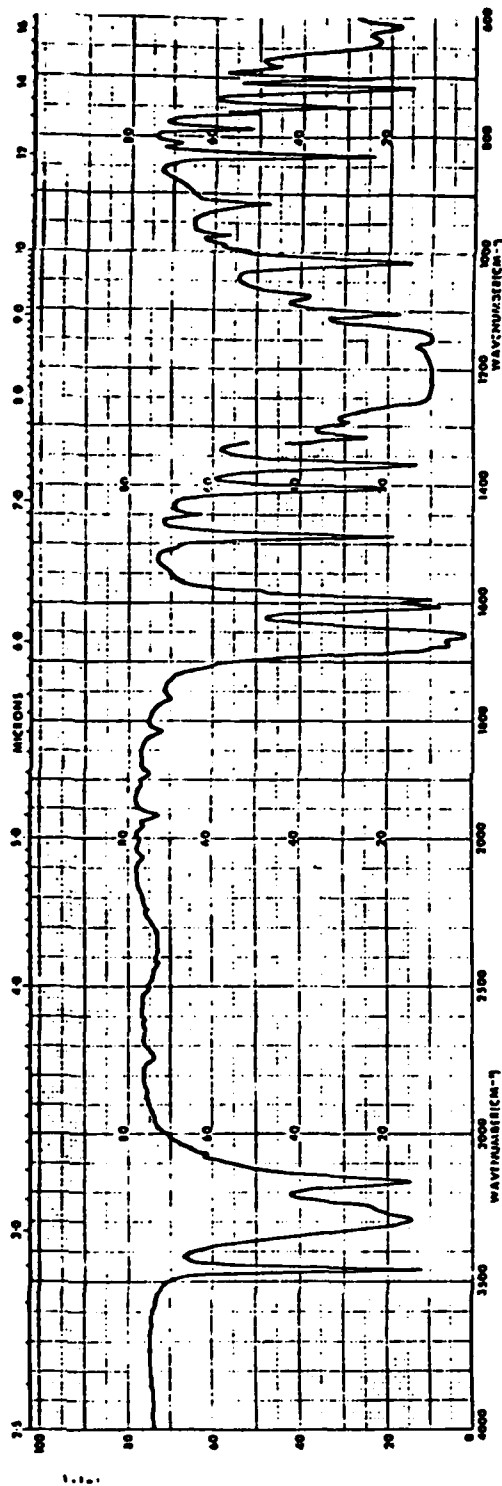
Figure 1: Infrared spectrum of N-phenyl-perfluoro-n-octylamidine (Kel-F/Nujol)
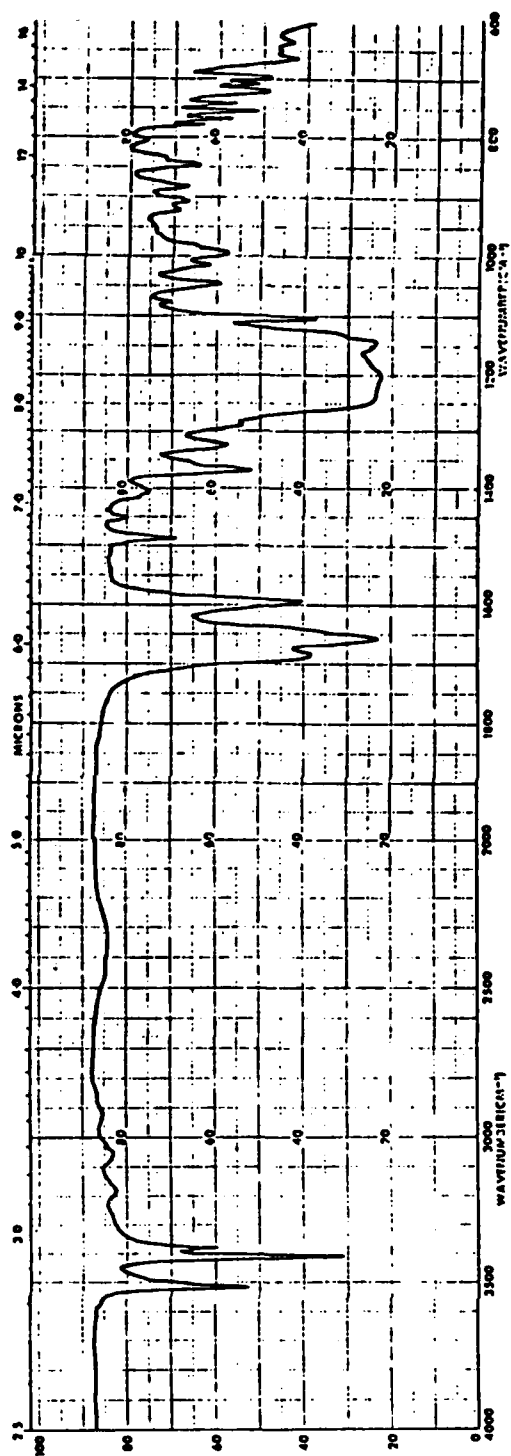
Figure 2: Infrared spectrum of N'-(perfluoro-n-octylimidoyl)-N-phenyl-perfluoro-n-octylamidine (Kel-F/Nujol)

n-octanonitrile in 2:1 mole ratio over an extended period at 90-115°C gave a mixture of products listed in Table 5. The compounds were identified and quantitated by GC/MS.

TABLE 5

Products obtained from the interaction of aniline and perfluoro-n-octanonitrile in 2:1 mole ratio at 90-115°C

Compound	Percent of product mix
$[C_7F_{15}CN]_3$	44.0
$C_7F_{15}C(=NH)NH\Phi$, XIII	9.8
$C_7F_{15}C(=NH)N=C(NH\Phi)C_7F_{15}$, XV	6.9
$C_7F_{15}C(=N\Phi)NH\Phi$, XIV	7.5
$C_7F_{15}C(=N\Phi)-N=C(NH\Phi)C_7F_{15}$, XVI	7.7

The origins of triazine, N-phenyl-perfluoro-n-octylamidine (XIII), and Compound XIV have been discussed above. The imidoyl-amidine (XV) must be produced by the addition of the nitrile to N-phenyl-perfluoro-n-octylamidine (XIII), i.e.,

$$C_7F_{15}\overset{\overset{\text{NH}}{\|}}{C}\text{-NH}\Phi \quad + \quad C_7F_{15}CN \quad \longrightarrow \quad C_7F_{15}\overset{\overset{\text{NH}}{\|}}{C}\diagdown_{N}\diagup\overset{\overset{\text{NH}\Phi}{|}}{CC_7F_{15}}$$

XIII

XV
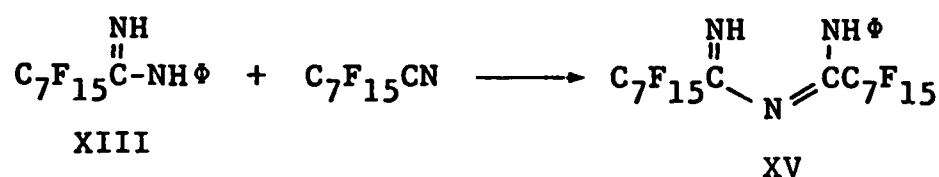
This was verified by its preparation and isolation from the reaction of amidine with perfluoro-n-octanonitrile. The occurrence of secondary reactions, even under these conditions, was evidenced by the presence of triazine. Such interconversions in systems containing or producing ammonia-nitrile-amidine and imidoylamidine were observed previously [3]. These processes would be expected to be more evident in reactions carried out

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at elevated temperatures for prolonged periods of time.

With respect to the product mix given in Table 5, there are three possible paths for the formation of the imidoylamidine, XVI, i.e.,

$$
\begin{array}{ccc}
& \overset{NH}{\underset{||}{}} & & \overset{N\Phi}{\underset{||}{}} & & \overset{NH}{\underset{||}{}} \quad \overset{NH\Phi}{\underset{|}{}} \\
(1) \ 2 \ R_fC\text{-}NH\Phi & & (2) \ R_fC\text{-}NH\Phi & & (3) \ R_fC\diagdown_{N}\diagup^{CR_f} \\
XIII & & XIV & & XV
\end{array}
$$

$$-NH_3 \qquad \downarrow +R_fCN \qquad +\Phi NH_2 \ -NH_3$$

$$R_fC\diagdown_{N}\diagup^{CR_f} \quad (\overset{N\Phi}{||} \quad \overset{NH\Phi}{|})$$

XVI
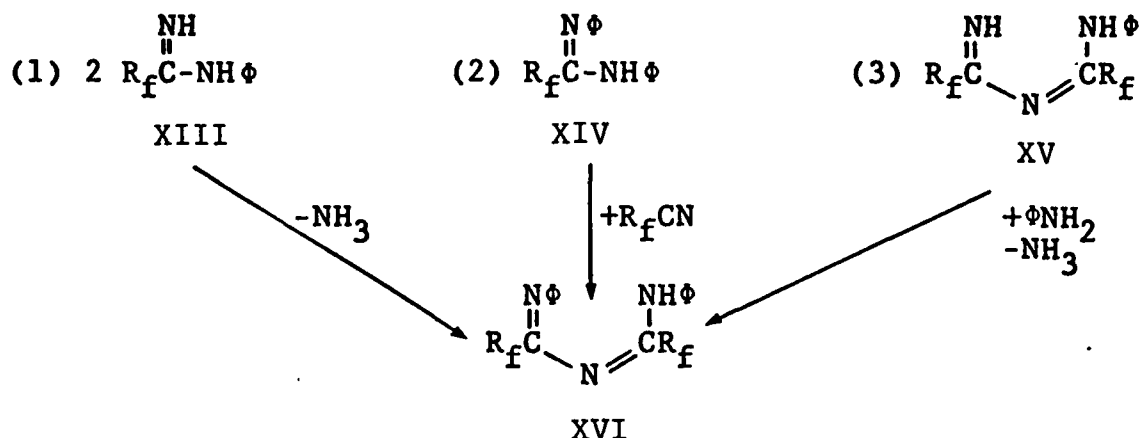
The first process is unlikely since after exposure at 200°C for 15 hr the amidine was recovered unchanged. Having an excess of aniline would favor process 3 rather than reaction 2. It should be noted that in the presence of acetonitrile at 50°C, the production of the imidoylamidine, XV, was enhanced; however, all the other products were also formed.

The only novel compounds, which could be isolated and fully characterized, were N-phenyl-perfluoro-n-octylamidine and N'-(perfluoro-n-octylimidoyl)-N-phenyl-perfluoro-n-octylamidine. All the other compounds were identified by their mass spectral breakdown patterns.

The fragmentation patterns of the amidines and imidoylamidines, Compounds XIII-XVI, were closely related. All the compounds showed a strong molecular ion and a fragment following a loss of fluorine. The ion corresponding to the loss of the perfluoroheptyl side chain constituted the base peak in all four compounds. Its formation from the molecular ion in the case of the two isolated compounds, N-phenyl-perfluoro-n-octylamidine, XIII, and N'-(perfluoro-n-octylimidoyl)-N-

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phenyl-perfluoro-n-octylamidine, XV, is shown by the metastables
at m/e 29 and 299.5, respectively, i.e.,

$$488^+(M) \longrightarrow 119^+ + 369[C_7F_{15}] \qquad m^* \quad 29.0$$

$$883^+(M) \longrightarrow 514^+ + 369[C_7F_{15}] \qquad m^* \quad 229.2$$
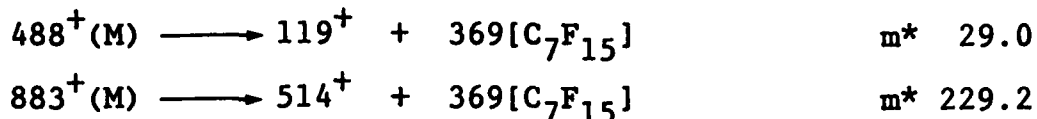
The imidoylamidines, XV and XVI, as well as the amidine, XIV,
had high intensity peaks at m/e 472^+ corresponding to the
$C_7F_{15}C=N\Phi$ fragment. This ion was absent in the mass spectrum
of N-phenyl-perfluoro-n-octylamidine.

3.7 Reactions of perfluoro-n-octanonitrile with phenylphosphine

As described in the preceding section, aniline was found
to add readily to perfluoro-n-octanonitrile giving N-phenyl-
perfluoro-n-octylamidine, N'-(perfluoro-n-octylimidoyl)-N-
phenyl-perfluoro-n-octylamidine, and the corresponding diphenyl-
analogues. Similar behavior was expected to be observed with
phenylphosphine.

Interactions of phenylphosphine and perfluoro-n-octano-
nitrile were carried out both neat and in solvents. The reac-
tions are summarized in Table 6.

TABLE 6

Interactions of perfluoro-n-octanonitrile and phenylphosphine[a]

	Reactants		Conditions			Partial Analysis		
Test No.	ΦPH_2 mmol	$C_7F_{15}CN$ mmol	Temp °C	Time hr	Solv.	ΦPH_2[b] %	R_fCN[c] %	Φ_4P_4[b] %
1	7.42	2.40	130	15	none	40	-	29
2	2.65	7.68	130	36	none	-	51	55
3	25.43	25.36	50	654	A/F[d]	n.d.	n.d.	52
4	1.33	12.66	130	24	none	-	84	42

a Tests 1,2,4 were performed in sealed tubes in vacuo; test 3 was carried out under
  nitrogen by-pass.
b Based on phenylphosphine employed.
c Based on perfluoro-n-octanonitrile employed.
d A 1:1, by volume, acetonitrile/Freon mixture was utilized.

The product mix depended strongly on the conditions employed. This is clearly evident from the data given in Figures 3-5. Under all the conditions studied, reduction was the major process. No "primary" adduct of phenylphosphine was detected. None of the products, with the exception of $C_7F_{15}CH_2NHC(C_7F_{15})=NH$ (XXIII)were isolated and characterized. All of the identifications are thus based solely on mass spectrometry.

As mentioned above, reductions by phenylphosphine, with concomittant formation of tetraphenyltetraphosphine,constituted one of the major processes taking place. This is clearly evident from the high yield of the isolated tetraphenyltetraphosphine shown in Table 6. Subsequent reactions of the reduced materials with perfluoro-n-octanonitrile and with each other gave rise to the wide spectrum of products found. A number of the reactions were accompanied by evolution of ammonia. This is proven by the nature of the compounds, formation of triazine, XXII, and in particular the presence of imidoylamidine, XXI [28].

The relatively simple products and the potential paths for their formation are presented in Table 7. The undetected, plausible compounds are those shown in brackets. Only three of the compounds listed were the adducts of phenylphosphine. Yet, under specific conditions, the individual compounds could be obtained in relatively good yields. For example, the yield of the phenylphosphine-dinitrile adduct, XXXI, increased from ~3% to 28% by changing the nitrile to phenylphosphine ratio from 0.3 to 10. It is believed that tailoring further the reaction conditions should permit its actual isolation.

The presence of solvent seemed to affect strongly the type of products formed. The production of the more complex compounds was kinetically controlled. This is clearly evident from the plots given in Figure 6. Initially at 50°C in acetonitrile/Freon-113 solvent mixture, the only material present, to a significant degree,was the reduced phenylphosphine adduct

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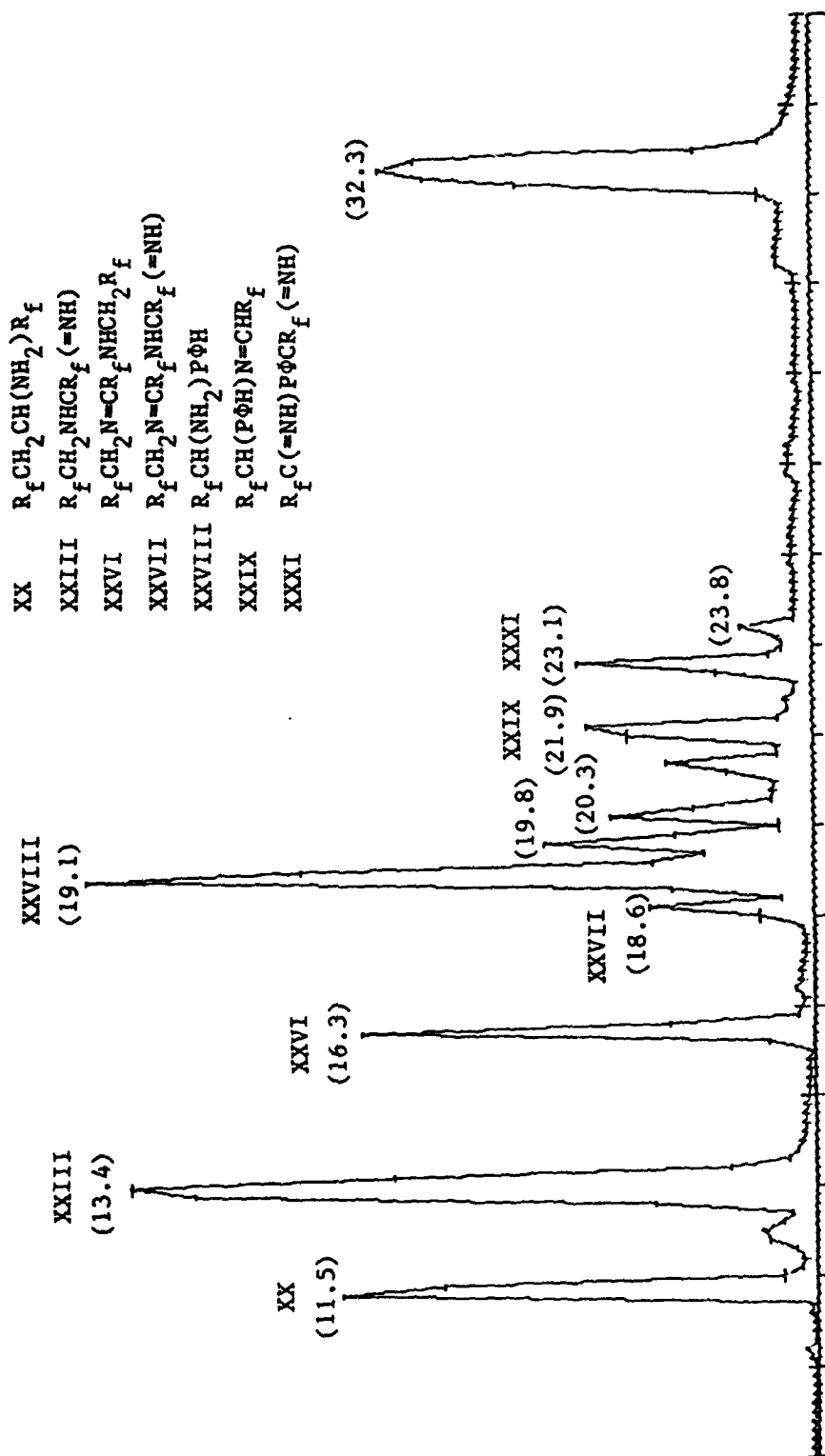
Figure 3 : Ion chromatogram of the product mix from the interaction of phenylphosphine and perfluoro-n-octanonitrile in a 3:1 mole ratio at 130°C for 15 hr.

XX	$R_f CH_2 CH(NH_2) R_f$
XXIII	$R_f CH_2 NHCR_f (=NH)$
XXVI	$R_f CH_2 N=CR_f NHCH_2 R_f$
XXVII	$R_f CH_2 N=CR_f NHCR_f (=NH)$
XXVIII	$R_f CH(NH_2) P\Phi H$
XXIX	$R_f CH(P\Phi H) N=CHR_f$
XXXI	$R_f C(=NH) P\Phi CR_f (=NH)$

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XVII $R_fCH=NH$
XVIII $R_fCH_2NH_2$
XIX $R_fCH=NCH_2R_f$
XXII $[R_fCN]_3$
XXIII $R_fCH_2NHCR_f(=NH)$
XXV $R_fCH=NCR_fNHCR_f(=NH)$
XXVII $R_fCH_2N=CR_fNHCR_f(=NH)$
XXXI $R_fC(=NH)PC_6H_5CR_f(=NH)$

XVII (3.3)

XVIII (4.5)

(9.6)

XIX (10.9)

XXII (13.6)

XXIII (14.4)

(15.6) (17.8)

XXV (19.0)

XXVII (19.7)

(20.5)

(21.0) (22.8)

XXXI (24.1)

Figure 4:   Ion chromatogram of the product mix from the interaction of phenylphosphine and Perfluoro-n-octanonitrile in a 1:10 mole ratio at 130°C for 24 hr.

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XVII $R_f CH=NH$

XIX $R_f CH=NCH_2 R_f$

XXIII $R_f CH_2 NHCR_f (=NH)$

XXI $R_f C(=NH)N=CR_f (NH_2)$

XXV $R_f CH=NCR_f=NCR_f (=NH)$

XXVIII $R_f CH(NH_2)P\Phi H$

XXIX $R_f CH(P\Phi H)N=CHR_f$

XXXIV $R_f CH(P\Phi H)NHCH=CFC_6 F_{13}$

XXXI $R_f C(=NH)P\Phi CR_f (=NH)$

XXXII $\overline{\Phi PCH(R_f)NHCH(R_f)P\Phi}$

XXXIII $\overline{\Phi PCH(R_f)NHCH(CFHC_6 F_{13})P\Phi}$

ΦPF_2 (9.0)

XVII (3.1)

(10.1)

XIX (10.7)

XXIII (13.9)

XXI (15.2)

XXV (17.0)

XXVIII (19.8)

XXIX (21.8)

(21.1)

XXXIV (22.4)

XXXI (23.9)

(25.1)

(26.3)

XXXIII (31.7)

XXXII (31.0)

(33.6)
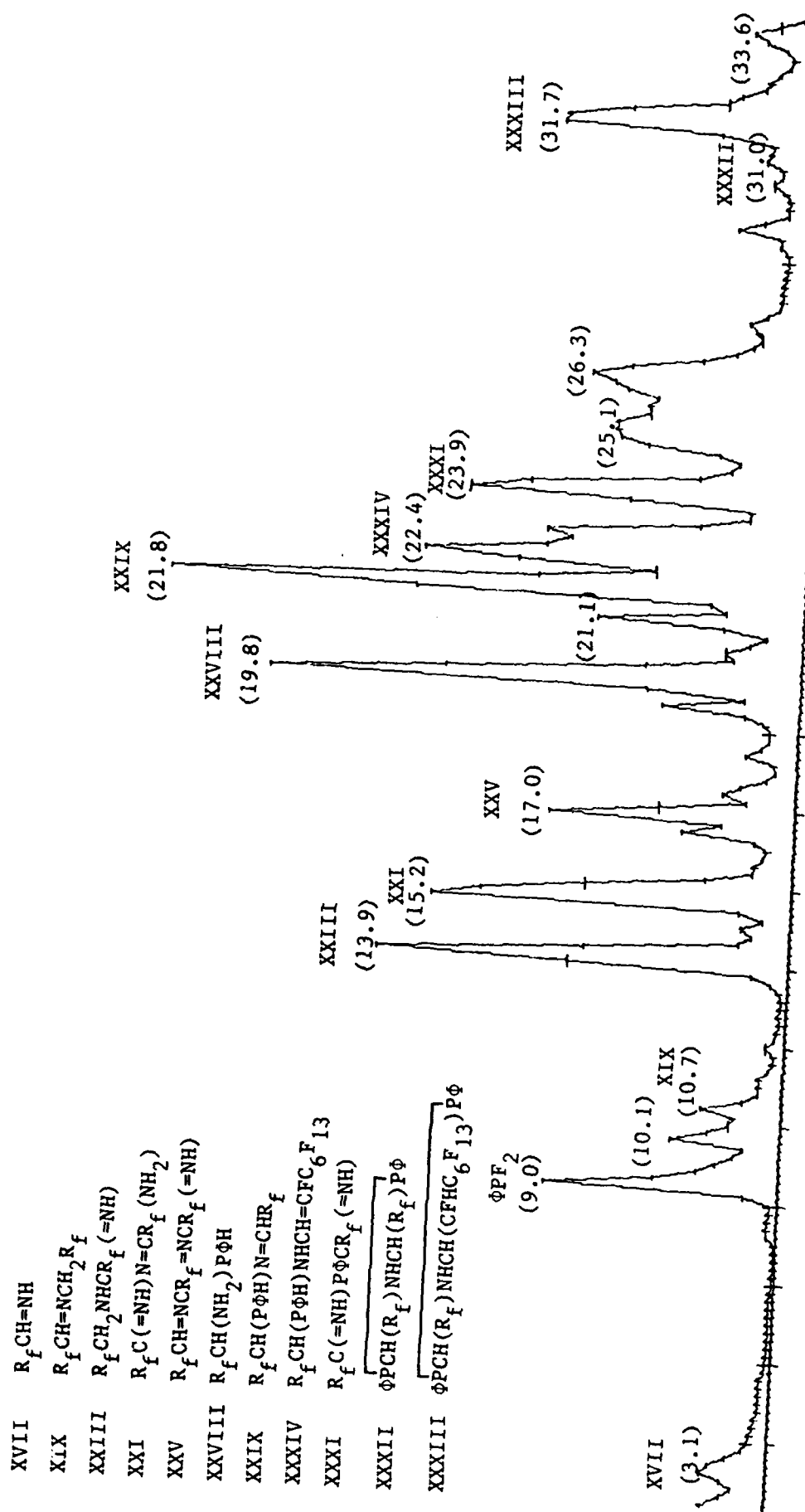
Figure 5: Ion chromatogram of the product mix from the interaction of phenylphosphine and perfluoro-n-octanonitrile in a 1:1 mole ratio at 50°C for 27 days (in solvent).

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Both of the adducts in their mass spectra exhibited an intense molecular ion; in the case of the adduct XXXV, the molecular ion constituted the base peak. Subsequent loss of the C_7F_{15}-chain from the molecular ion resulted in the 212^+ ion, shown by the metastable at m/e 77.4, i.e.,

$$581^+(M) \longrightarrow 212^+ + 369[C_7F_{15}] \qquad m^* \ 77.4$$
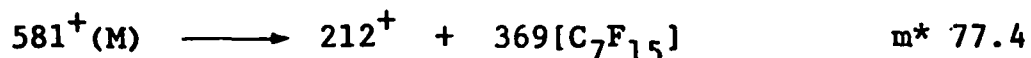
The ion m/e 214 responsible for the loss of the perfluoroheptyl unit in adduct XXXVI is only of low intensity, 3.6%. The high intensity ions m/e 398^+, 378^+, and 371^+ are all involving the loss of the $(C_6H_5)_2P$ fragment, i.e.,

$$M \ (583) \longrightarrow 398^+ + (C_6H_5)_2P$$

$$M \ (583) \longrightarrow 378^+ + (C_6H_5)_2P + HF$$

$$M \ (583) \longrightarrow 371^+ + (C_6H_5)_2P + HCN$$
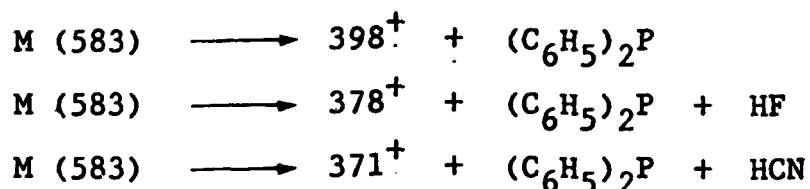
For none of these processes were metastables observed, thus the breakdown path is unknown. The base peak, 186^+, diphenylphosphine ion, is formed from the molecular ion, i.e.,

$$583^+(M) \longrightarrow 186^+ + 397[C_7F_{15}CH=NH] \qquad m^* \ 59.3$$
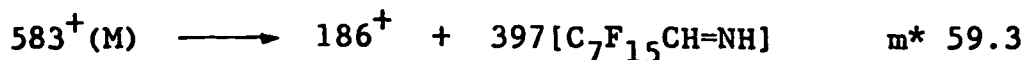
It should be noted that this breakdown is the reverse of the postulated formation of adduct XXXVI via the imine intermediate XVII. Further breakdown of the 186^+ ion to the 108^+ ion occurs in both of the adducts as shown by a metastable at m/e 62.7.

the saturated adduct is not formed by reduction of the primary adduct XXXV. Treatment of adduct XXXV with diphenylphosphine, under conditions when the reduced product was produced from nitrile and diphenylphosphine, failed to result in its formation. The presence of the imine, $C_7F_{15}CH=NH$, unequivocally identified in test 7 and found also in the reactions of phenylphosphine with perfluoro-n-octanonitrile, discussed earlier, indicates that formation of the "reduced adduct" proceeds via this intermediate, i.e.,

$$C_7F_{15}C\equiv N \ + \ 2(C_6H_5)_2PH \longrightarrow C_7F_{15}CH=NH + (C_6H_5)_2PP(C_6H_5)_2$$
$$XVII$$
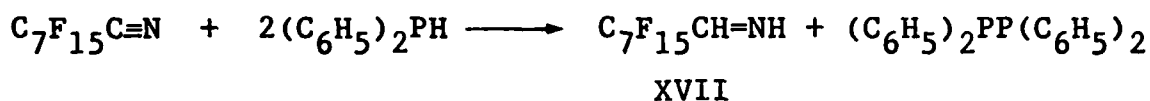
No other nitrile reduction products were detected. It is thus postulated that the initially formed imine XVII reacts with an additional molecule of diphenylphosphine giving the adduct XXXVI. The infrared spectrum presented in Figure 8 with the doublet at 3359 and 3435 cm^{-1} confirms the presence of an NH_2 group.

Inasmuch as the primary adduct XXXV does not add a second molecule of diphenylphosphine and since it is not reduced by diphenylphosphine, one is tempted to speculate that the reduction is due to initial addition of the diphenylphosphorus moiety onto nitrogen, i.e.,

$$C_7F_{15}C\equiv N \ + \ (C_6H_5)_2PH \longrightarrow [C_7F_{15}CH=NP(C_6H_5)_2]$$
$$XXXVII$$
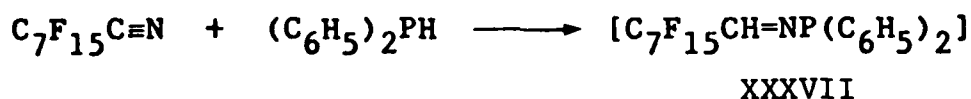
The Compound XXXVII, being unstable, reacts then with another molecule of diphenylphosphine giving the imine and tetraphenyldiphosphine, i.e.,

$$[C_7F_{15}CH=NP(C_6H_5)_2] \ + \ (C_6H_5)_2PH \longrightarrow C_7F_{15}CH=NH + (C_6H_5)_2PP(C_6H_5)_2$$
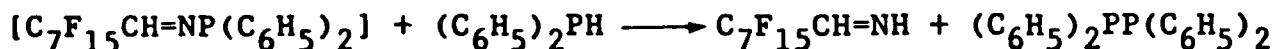
The prevention of the reduction by trace quantities of water supports the above mechanism, since both the formation of Compound XXXVII and its addition complex with diphenylphosphine would be expected to be disrupted by an ionic mechanism.

43
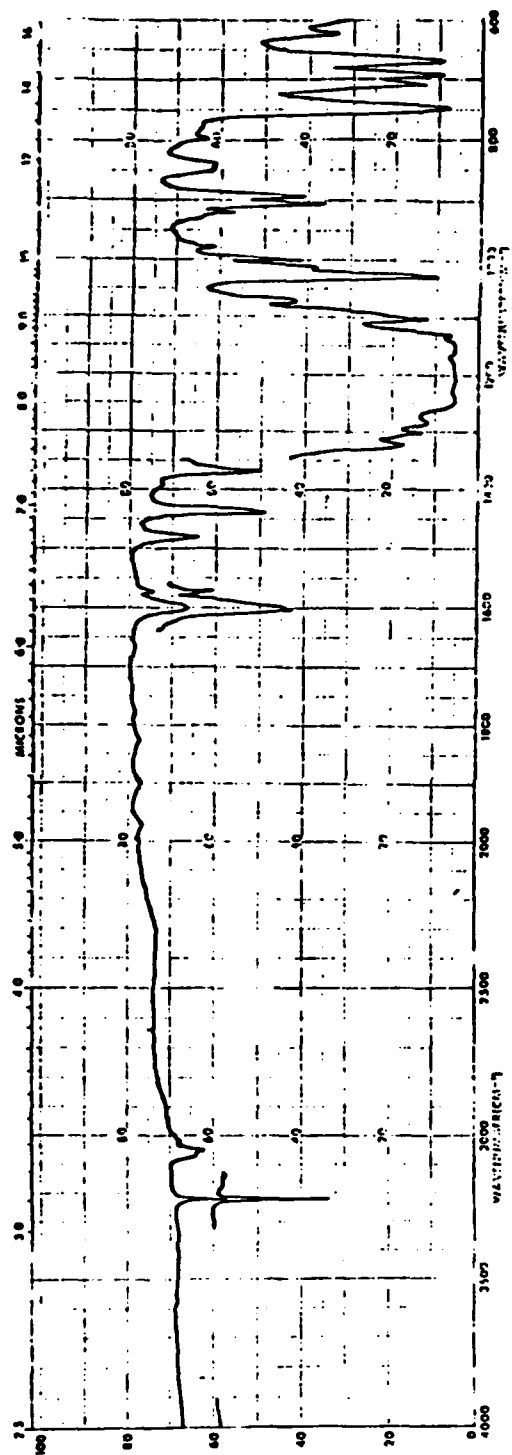
Figure 7: Infrared spectrum of $C_7F_{15}C(=NH)P(C_6H_5)_2$ (Kel-F/Nujol)
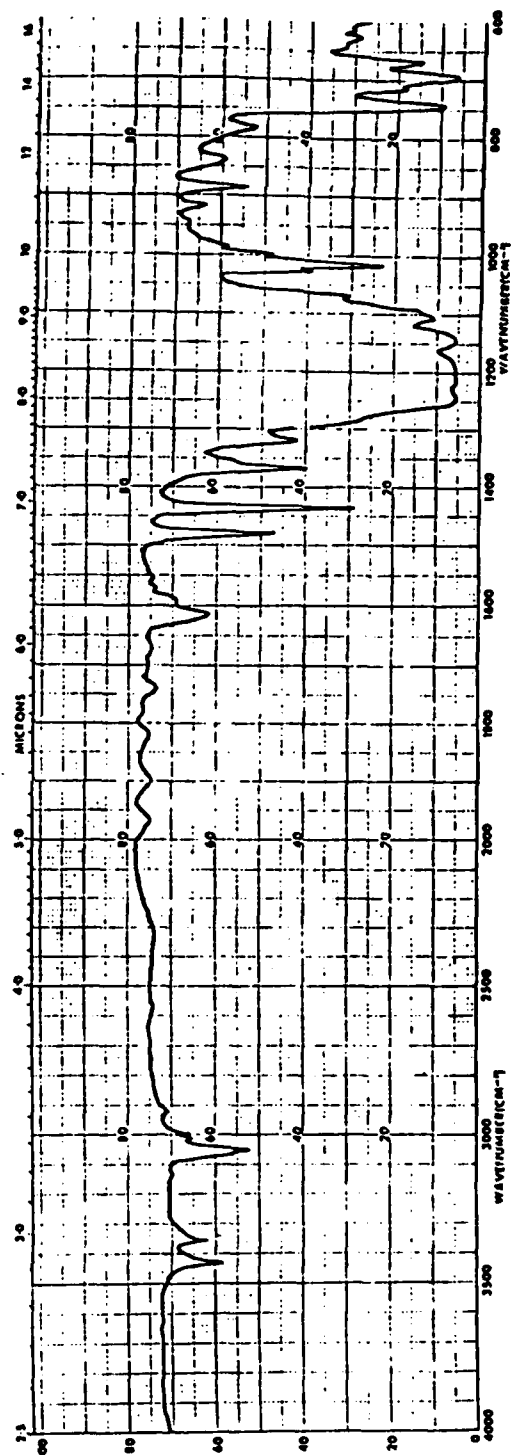
Figure 8: Infrared spectrum of $C_7F_{15}CH(NH_2)P(C_6H_5)_2$ (Kel-F/Nujol)

TABLE 8

Results of interactions of equimolar quantities of diphenylphosphine and perfluoro-n-octanonitrile[a]

Test No.	Reaction conditions			Compounds; relative ratios[b]				
	Solv.[c]	Temp °C	Time days	R_fCN	ϕ_2PH	ϕ_2POF	$R_f(=NH)P\phi_2$	$R_fCH(NH_2)P\phi_2$
10	none	50	1.35	91.2[d] (0.04)[d]	0.4 (87.3)	— (0.4)	5.0 (3.3)	1.4 (1.8)
2	none	100	1.25	48.2[d] (1.7)[d]	10.3 (66.8)	? (5.4)	9.7 (7.7)	.17.8 (18.4)
5	A/F 2:1	50	5	n.d.	1	0.3	0.1	0.6
7	A	40	13	n.d.	1	0.1	0.6	0.4
3	A/F 2:3	50	14	n.d.	1	1	?	17.9
9[e]	A/F 2:3	50	12	n.d.	1	4.3	12.4	—

a In these experiments, the typical concentration used was ∿5 mmol of each of the two reagents per 10 ml of solvent(s). All the reactions were carried out either under nitrogen by-pass or in an inert atmosphere enclosure.
b These are based on gas chromatographic area ratios.
c The solvents used were acetonitrile (A) and Freon-113 (F); the solvent ratios given are volume ratios.
d The two sets of values correspond to concentrations in bottom (upper numbers) and top (lower numbers in parentheses) layers, respectively, since the reaction mixture was immiscible.
e In this test, a trace of water was added.

The formation of the primary adduct is a straight-forward process, i.e.,

$$(C_6H_5)_2PH \quad + \quad C_7F_{15}CN \quad \longrightarrow \quad C_7F_{15}\overset{\overset{NH}{\|}}{C}P(C_6H_5)_2$$

XXXV
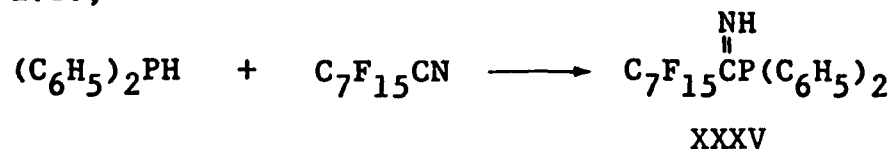
The composition was in agreement with the elemental analysis and was further confirmed by the mass spectral fragmentation patterns. The hydrogen bonded NH is indicated by the band at 3220 cm^{-1}, whereas the absorption at 1600 cm^{-1} is in agreement with the presence of the C=N group, as shown in Figure 7.

With respect to the reduced adduct, XXXVI, the overall process can be represented by:

$$3(C_6H_5)_2PH + C_7F_{15}CN \longrightarrow C_7F_{15}\overset{\overset{NH_2}{|}}{C}HP(C_6H_5)_2 + (C_6H_5)_2PP(C_6H_5)_2$$

XXXVI
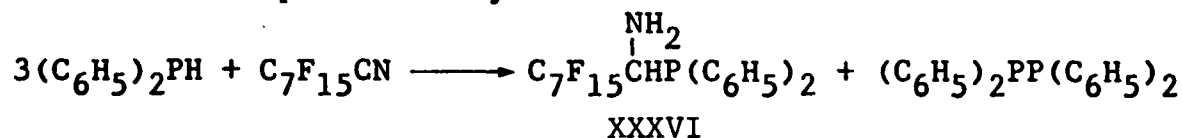
Based on the data available, it is almost certain that

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Compound XXXI has a completely different arrangement from the previous two materials. Again, the fragmentation is in total agreement. Ions 900^+[M], 881^+[M - 19(F)], and 531^+[M - 369(C_7F_{15})], although in support of the structure, do not really confirm it. However, the absence of the M - P(C_6H_5) or M - P(C_6H_5)H ions, in conjunction with the base peak at m/e 108^+-[C_6H_5P] and the presence of the 135^+ ion [$C_7F_{15}C=NH$], absent in Compounds XXVIII and XXIX, prove the validity of the postulated arrangement. It should be noted that the infrared spectrum of the product mixture containing 50% of Compound XXXI provided further proof of the structure, based on the absence of P-H absorption at 2300 cm^{-1}.

3.8 Reactions of perfluoro-n-octanonitrile with diphenylphosphine

As discussed in the preceding section, the addition of phenylphosphine to perfluoro-n-octanonitrile was found to be invariably associated with reduction of the nitrile. It was thus of interest to determine whether diphenylphosphine would behave analogously to phenylphosphine or whether the presence of the two phenyl groups would measurably lower the reduction action.

Diphenylphosphine and perfluoro-n-octanonitrile are virtually immiscible. Yet, even in the absence of solvent, interaction did occur as evident from the data given in Table 8. It should be noted that all the reactions were monitored by GC/MS. In the majority of tests, both the primary and reduced adducts were formed. In the absence of solvent, the higher temperature favored the reduced product (compare tests 10 and 2). The presence of acetonitrile/Freon-113 solvent mixture, in the absence of water, resulted in an essentially exclusive production of the reduced adduct, whereas having a trace of water gave only the primary adduct.

The presence of a molecular ion facilitates greatly structure determination. Thus, for $C_7F_{15}CH_2NHC(C_7F_{15})=NH$, the composition could be easily deduced from the ions: $794^+[M]$, $775^+[M - 19(F)]$, $475^+[M - 319(C_6F_{13})]$, and $425^+[M - 369(C_7F_{15})]$. However, in the case of the other compounds such as XXVI, molecular weight 1176, beyond the mass spectrometer/computer range of m/e 1066, assignment was based both on GC retention times and the characteristic fragmentation patterns. In this type of compound, the breakdown is dominated by the loss of the C_7F_{15} side chain shown here by the 807^+ ion. The same applies to Compound XXVII, molecular weight 1189, where again the base peak, m/e 820, was formed by the loss of the perfluoroheptyl chain. Similar reasoning led to the identification of Compound XXV of molecular weight 1187. Here the 818^+ ion corresponded to the loss of the C_7F_{15} chain.

The products containing the C_6H_5P moiety all had molecular weights within the range of the mass spectrometer system. Furthermore, each material did form a relatively high intensity molecular ion. This made the composition determination relatively easy. In all the adducts, it is postulated that phosphorus resides on carbon not nitrogen. This is based primarily on the work with diphenylphosphine which is discussed in the next section of this report.

The fragmentation pattern of $C_7F_{15}CH(NH_2)P(C_6H_5)H$, XXVIII, namely the molecular ion 507^+, $398^+[M - 109(P(C_6H_5)H)]$, 110^+ $[P(C_6H_5)H_2]$, $79^+(CF_2CHNH_2)$, and $28^+[CH=NH]$, are fully consistent with the postulated arrangement. The same applies to compound XXIX, i.e., $887^+[M]$, $868^+[M - 19(F)]$, $778^+[M - 109(P(C_6H_5)H)]$, $568^+[M - 319(C_6F_{13})]$, $501^+[M - 386(C_7F_{15} + NH_3)]$, $490^+[M - 397(C_7F_{15} + CH=NH)]$, $410^+[M - 477(C_7F_{15} + PC_6H_5)]$, $109^+[P(C_6H_5)H]$, $90^+[CF_2CH_2CN]$, and $28^+[CH=NH]$. With respect to the location of the $P(C_6H_5)H$ group on carbon not nitrogen, the ions 501^+ and 490^+ support strongly the structure proposed.

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Regarding Compound XXXIV, unfortunately the fragmentation pattern does not provide sufficient information to completely support or eliminate from consideration either structure XXXIVa or XXXIVb. The ion $760^+[M - 109(C_6H_5PH)]$, which constitutes the base peak, does prove the presence of C_6H_5PH substituent, whereas the ion $472^+[M - 397(C_7F_{15} + CH=NH)]$ tends to indicate that C_6H_5PH is located on the carbon to which is attached the $CFHC_6F_{13}$ side chain. On the other hand, the $491^+[M - 378(C_7F_{14} + CH=NH)]$ ion would favor the arrangement XXXIVb.

The mass spectral breakdown patterns of the compounds listed in Table 7 are relatively easy to assign. The isomerism due to proton location is to be expected with analogy to the amidine and imidoylamidine type of arrangements derived from interactions of ammonia and perfluoroalkyl nitriles. Thus, for instance, XXIII can be depicted in either form:

$$R_fCH_2NHC(R_f)=NH \rightleftharpoons R_fCH_2N=C(R_f)NH_2$$
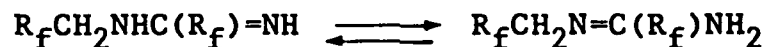
This, however, will not affect the fragmentation patterns and for ease of presentation, only one form has been used.

Although no molecular ions were registered for the two primary nitrile reduction products, $C_7F_{15}CH=NH$, XVII, and $C_7F_{15}CH_2NH_2$, XVIII, the presence in the mass spectrum of $C_7F_{15}CH=NH$ of $378^+[M - 19(F)]$, $78^+[CF_2CH=NH]$, and $28^+[CH=NH]$, supported by the GC retention time, proves the composition beyond any doubt. The same applies to $C_7F_{15}CH_2NH_2$, XVIII, based on $398^+[M - 1(H)]$, $380^+[M - 19(F)]$, $79^+[CF_2CHNH_2]$, and $30^+[CH_2NH_2]$. Material XIX also did not form a molecular ion; however its breakdown pattern was in total agreement with the structural assignment, i.e., $760^+[M - 19(F)]$, $410^+[M - 369(C_7F_{15})]$, and $28^+[CH=NH]$. Only a very low intensity (1.1%) molecular ion, 781^+, was registered for $C_7F_{15}CH(NH_2)CH_2C_7F_{15}$, but again the fragmentation pattern $762^+[M - 19(F)]$, $412^+[M - 369(C_7F_{15})]$ confirmed the structural arrangement.

$$C_6F_{13}CF_2CH(NH_2)P(C_6H_5)H \quad + \quad H_2NCH_2CF_2C_6F_{13}$$

$$\downarrow \begin{array}{l} -NH_3 \\ -HF^3 \end{array}$$

XXXIVa   or   XXXIVb
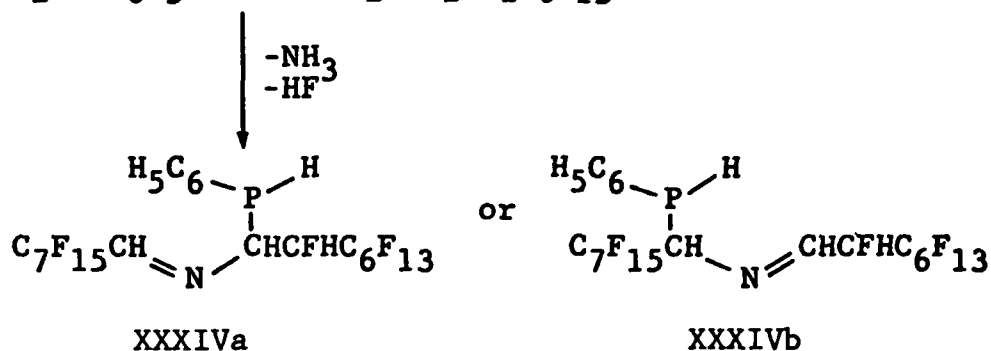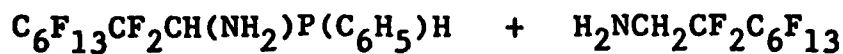
It must be understood that both the proposed mechanisms and structural arrangements are highly speculative; however, at least in the case of Compound XXXIII, the structural assignment, based on the fragmentation pattern, is well grounded. This is true both with respect to breakdown pattern similarity to that of Compound XXXII, discussed above, as well as with respect to the GC retention time.

In analogy to Compound XXXII, this material also exhibits in its mass spectrum a very intense molecular ion, 977^+, which here actually constitutes the base peak. Loss of fluorine then gives the 958^+ ion. However, of particular interest here are the ions m/e 626^+, 608^+, 598^+, and 580^+, which correspond to the loss of either of the two side chains, namely C_7F_{15} and $CHFC_6F_{13}$, and thus confirm the proposed arrangement, i.e.,

$$M(977) \longrightarrow 626^+ \quad + \quad 351 \; [CFHC_6F_{13}]$$
$$M(977) \longrightarrow 608^+ \quad + \quad 369 \; [C_7F_{15}]$$
$$M(977) \longrightarrow 598^+ \quad + \quad 379 \; [CFHC_6F_{13} + CH=NH]$$
$$M(977) \longrightarrow 580^+ \quad + \quad 397 \; [C_7F_{15} + CH=NH]$$
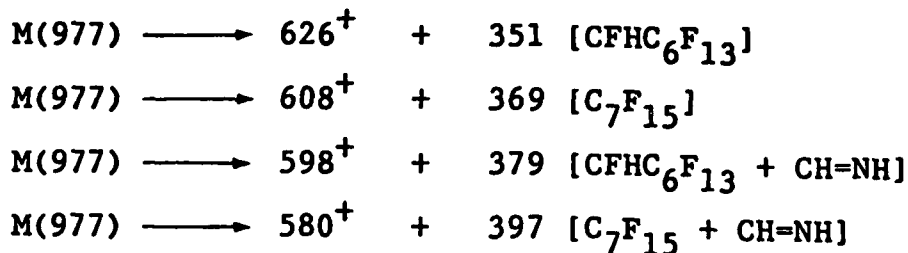
In the same manner as in Compound XXXII, here also the presence of the diphosphine unit, $C_6H_5PPC_6H_5$, is shown by the ions $422^+[M - C_6H_5PPC_6H_5 - C_6F_{13}]$, $229^+[(C_6H_5)PP(C_6H_5)CH]$, $217^+[C_6H_5PPC_6H_5(H)]$, and $216^+[C_6H_5PPC_6H_5]$.

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are straightforward inasmuch as the structures involved are reasonably simple. Structural assignment for XXXII is, however, definitely more complex. Here, the intense ions in the high mass region are fully supportive of the postulated structure. Loss either from the molecular ion, 995^+, or from the neutral molecule of a fluorine atom gives m/e 976, whereas the loss of the C_7F_{15} side chain gives the 626^+ ion. The subsequent loss of CH=NH moiety, 598^+, confirms the R_fCH-NH arrangement. The presence of the diphosphine unit $C_6H_5PPC_6H_5$ is proven by the ions 460^+, 410^+, and 390^+, i.e.,

$$M(995) \longrightarrow 460^+ + 535 \ [C_6H_5PPC_6H_5 + C_6F_{13}]$$

$$M(995) \longrightarrow 410^+ + 585 \ [C_6H_5PPC_6H_5 + C_7F_{15}]$$

$$M(995) \longrightarrow 390^+ + 605 \ [C_6H_5PPC_6H_5 + C_7F_{15} + HF]$$
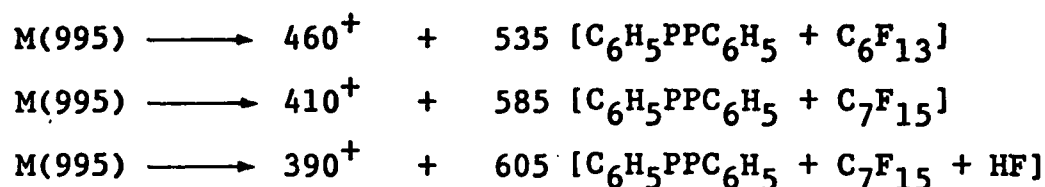
as well as the $C_6H_5PPC_6H_5(H)^+$, m/e 217, and the $C_6H_5PPC_6H_5^+$, m/e 216, ions.

The origin of Compounds XXXIII and XXXIV is more obscure than that of XXXII. Yet, the paths leading to the two materials must be related. Potential mechanisms are depicted below:

$$2 \ C_6F_{13}CF_2CH(NH_2)P(C_6H_5)H$$

XXXIII

XXVIII. However, as time progressed, the secondary or rather tertiary products started to appear. The complexity of the product mix after 654 hr (27 days) exposure is illustrated by the ion chromatogram presented in Figure 5. It should be pointed out that in the ion chromatogram the concentration of Compound XXIX appears to be higher than that of XXVIII; however, the opposite is true using flame ionization, which is believed to be much more reliable in concentration determinations.

Compounds XXXII, XXXIII, and XXXIV have not been detected in the tests performed in the absence of solvent. The material with a retention time of 32.3 min in Figure 3 has not been identified; it does, however, contain one or more phenylphosphine substituents. Regarding Compound XXXII, it could be formed by either of the paths delineated below:

$\{R_fC[P(C_6H_5)H]=NH\}$ + $R_fCH(NH_2)P(C_6H_5)H$

XXX   XXVIII

$\downarrow$ $-NH_3$

$$\left[\begin{array}{c} H_5C_6 \diagdown P \diagup H \quad H \diagdown P \diagup C_6H_5 \\ H \diagup \quad C \quad \diagdown \quad C \diagdown R_f \\ R_f \diagup \quad N \quad \diagdown \end{array} \right] \longrightarrow \begin{array}{c} H_5C_6 \quad C_6H_5 \\ H \diagdown P \!\!-\!\! P \diagup H \\ C \quad \quad C \\ R_f \quad N \quad R_f \\ H \end{array}$$

XXXII

$\uparrow$

$+C_6H_5PH_2$
$-NH_3$

$R_fCH(NH_2)P(C_6H_5)H$ + R_fCN $\longrightarrow$ $\{R_fCH[P(C_6H_5)H]N=CR_f(NH_2)\}$

XXVIII

The mass spectral assignments for the majority of the compounds listed in Table 7 will be discussed later. These

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Figure 6: Semi-log plot of concentration versus time for products from the reaction of phenyl-phosphine and perfluoro-n-octanonitrile at 50°C in acetonitrile/Freon-113

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TABLE 7

Compilation of reactions leading to specific products obtained on
interaction of phenylphosphine and perfluorooctanonitrile[a]

$$R_f CN \;+\; C_6H_5PH_2 \longrightarrow R_f CH=NH \;+\; \tfrac{1}{4}(C_6H_5P)_4$$
$$\text{XVII}$$

$$R_f CN \;+\; 2\,C_6H_5PH_2 \longrightarrow R_f CH_2NH_2 \;+\; \tfrac{1}{4}(C_6H_5P)_4$$
$$\text{XVIII}$$

$$\underset{\text{XVII}}{R_f CH=NH} \;+\; \underset{\text{XVIII}}{R_f CH_2NH_2} \longrightarrow \underset{\text{XIX}}{R_f CH=NCH_2R_f} \;+\; NH_3$$

$$\underset{\text{XVIII}}{2\,R_f CH_2NH_2} \longrightarrow \underset{\text{XX}}{R_f CH_2CH(NH_2)R_f} \;+\; NH_3$$

$$2\,R_f CN \;+\; NH_3 \longrightarrow R_f C(=NH)N=CR_f(NH_2)$$
$$\text{XXI}$$

$$R_f CN \;+\; NH_3 \longrightarrow 1/3(R_f CN)_3 \;+\; NH_3$$
$$\text{XXII}$$

$$\underset{\text{XVIII}}{R_f CH_2NH_2} \;+\; R_f CN \longrightarrow \underset{\text{XXIII}}{R_f CH_2NHCR_f(=NH)}$$

$$\underset{\text{XVII}}{R_f CH=NH} \;+\; R_f CN \longrightarrow \underset{\text{XXIV}}{(R_f CH=NCR_f(=NH))}, \text{ n.i.}^{[b]}$$

$$\underset{\text{XVII}}{R_f CH=NH} \;+\; 2\,R_f CN \longrightarrow \underset{\text{XXV}}{R_f CH=NCR_f=NCR_f(=NH)}$$

$$\underset{\text{XXIII}}{R_f CH_2N=CR_f(NH_2)} \;+\; \underset{\text{XVIII}}{H_2NCH_2R_f} \longrightarrow \underset{\text{XXVI}}{R_f CH_2N=CR_fNHCH_2R_f} \;+\; NH_3$$

$$\underset{\text{XXIII}}{R_f CH_2N=CR_f(NH_2)} \;+\; R_f CN \longrightarrow \underset{\text{XXVII}}{R_f CH_2N=CR_fNHCR_f(=NH)}$$

$$\underset{\text{XVII}}{R_f CH=NH} \;+\; C_6H_5PH_2 \longrightarrow \underset{\text{XXVIII}}{R_f CH(NH_2)P(C_6H_5)H}$$

$$\underset{\text{XXIII}}{R_f CH(NH_2)P(C_6H_5)H} \;+\; HN=CHR_f \longrightarrow \underset{\text{XXIX}}{R_f CH[P(C_6H_5)H]N=CHR_f} \;+\; NH_3$$

$$R_f CN \;+\; C_6H_5PH_2 \longrightarrow \underset{\text{XXX}}{(R_f C[P(C_6H_5)H]=NH)}, \text{ n.i.}$$

$$2\,R_f CN \;+\; C_6H_5PH_2 \longrightarrow R_f C(=NH)P(C_6H_5)CR_f(=NH)$$
$$\text{XXXI}$$

a) R_f corresponds to C_7F_{15}.
b) Not identified.

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26.   H. C. Brown, Synthesis of Semi-Inorganic Fluorine Polymers.
        Part III. Perfluoroalkyl-Triazine Polymers. Studies of
        Intermediate Polymer Formation, Mechanism of Polymeriza-
        tion, and Catalytic Trimerization of Perfluoroalkyl
        Nitriles, WADC TR-59-272, Part III, August 1961.

27.   W. L. Reilly and H. C. Brown, J. Org. Chem., 22, 698
        (1957).

28.   H. C. Brown and P. D. Schuman, J. Org. Chem., 28, 1122
        (1963).

5. PRESENTATIONS, PUBLICATIONS, AND PATENTS

1.   Metals and Inhibitors Effects on Thermal Oxidative Degradation Reactions of Perfluoroalkylethers, Sixth Winder Fluorine Conference, Daytona Beach, Florida, February 1983.

2.   Functional Phospha-s-Triazines, Seventh Winter Fluorine Conference, Orlando, Florida, February 1985.

3.   Phospha-s-Triazines. VIII. Chloro-Substituted Diphospha-s-Triazines. Accepted for publication by the Journal of Fluorine Chemistry.

4.   Phospha-s-Triazines. IX. Chloro-Substituted Monophospha-s-Triazines. Accepted for publication by the Journal of Fluorine Chemistry.

5.   Phospha-s-Triazines. X. Thiophenyl-Substituted Phospha-s-Triazines. Accepted for publication by the Journal of Fluorine Chemistry.

6.   Reactions of Perfluoronitriles. I. Interactions with Aniline. Submitted to the Journal of Fluorine Chemistry.

7.   Reactions of Perfluoronitriles. II. Interactions with Phenylphosphine. Submitted to the Journal of Fluorine Chemistry.

8.   Reactions of Perfluoronitriles. III. Interactions with Diphenylphosphine. Submitted to the Journal of Fluorine Chemistry.

9.   Patent disclosure, Halo-Substituted Diphospha-s-Triazines and Their Derivatives, Air Force Invention No. 16303.

10.   Patent disclosure, Dihalo-Monophospha-s-Triazines and Their Derivatives, Air Force Invention No. 16,304.

A P P E N D I X

Experimental Details and Procedures
pertaining to the work carried out
from 1 March 1984 to 28 February 1985

GENERAL

All solvents used were reagent grade and were dried and distilled prior to use. Operations involving moisture or air sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B), under nitrogen by-pass, or in vacuo. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means.

Infrared spectra were recorded either neat (on liquids) or as double mulls (Kel-F oil No. 10 and Nujol) using a Perkin-Elmer Corporation infrared spectrophotometer Model 1330. The mass spectrometric analyses were obtained employing a DuPont 21-491B double focusing mass spectrometer attached to a Varian Aerograph Model 2700 gas chromatograph (GC), equipped with a flame ionization detector, and a DuPont 21-094 data acquisition and processing system. Gas chromatography was performed employing a 10' x 1/8" stainless steel column packed with 4% OV-101 on 80/100 mesh Chromosorb G using a programming rate of 8°C/min from 50-300°C. The molecular weights were determined in hexafluorobenzene using a Mechrolab Model 302 vapor pressure osmometer. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Interaction of perfluoro-n-octanonitrile with aniline; products mass spectra given in Table A-1.

(a) In 2:1 ratio at 120-140°C in a sealed tube

A mixture of perfluoro-n-octanonitrile (3.07 g, 7.77 mmol) and aniline (263 mg, 2.82 mmol) was heated in an evacuated, sealed ampoule at 120-140°C for 13 hr. Vacuum line fractionation gave ammonia (11.8 mg) and aniline (60.1 mg, 23% recovery). The involatile residue consisted of perfluoro-n-heptyltriazine and N-phenyl-perfluoro-n-octylamidine. A portion (470 mg) of the latter, mp 107-110°C, could be separated from the bulk

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of the triazine by recrystallization from hexane and repeated partitions in benzene.

(b) In a 1:2 mole ratio at 90-115°C under nitrogen by-pass

A stirred mixture of perfluoro-n-octanonitrile (3.00 g, 7.59 mmol) and aniline (1.25 g, 13.44 mmol) was heated at 92-115°C under nitrogen by-pass for 235 hr. Vacuum line fractionation gave aniline (1.07 g, 86% recovery) and perfluoro-n-octanonitrile (1.40 g, 47% recovery). The involatile residue, based on GC/MS, consisted of: $(C_7F_{15}CN)_3$, 44%; $C_7F_{15}C(=NH)N\Phi H$, 10%; $C_7F_{15}C(=NH)N=C(N\Phi H)C_7F_{15}$, 7%; $C_7F_{15}C(=N\Phi)N\Phi H$, 8%; and $C_7F_{15}C(=N\Phi)N=C(N\Phi H)C_7F_{15}$, 8%.

(c) Equimolar ratio in 1:1 acetonitrile/Freon-113 mixture at 50°C

A solution of perfluoro-n-octanonitrile (2.04 g, 5.16 mmol) and aniline (0.47 g, 5.05 mmol) in 10 ml of 1:1 acetonitrile/Freon-113 was stirred at room temperature for five days. The extent of reaction was very low as shown by GC. The rate at 50°C was higher by a factor of 5 as measured by the ratio of amidine to aniline. After 41 days at 50°C, the ratio of aniline:triazine:amidine:imidoylamidine was 1:0.5:2.9:1.2. Out of the reaction mixture, N-phenyl-perfluoro-n-octylamidine (0.64 g, 26% yield), mp 111-112°C), crystallized out. Anal. calcd. for $C_{14}H_7F_{15}N_2$: C, 34.44; H, 1.45; F, 58.37; N, 5.74; MW, 488.20. Found: C, 33.75; H, 1.39; F, 58.69; N, 6.07; MW, 500.

Thermal treatment of N-phenyl-perfluoro-n-octylamidine

A 91.3 mg sample of N-phenyl-perfluoro-n-octylamidine, in an evacuated ampoule, was subjected to stepwise heat treatment: 16 hr at 120°C; 38 hr at 150°C; and 15 hr at 200°C. Unchanged starting material was recovered.

Preparation of N'-(perfluoro-n-octylimidoyl)-N-phenyl-perfluoro-n-octylamidine

A solution of N-phenyl-perfluoro-n-octylamidine (1.45 g, 2.97 mmol) and perfluoro-n-octanonitrile (2.44 g, 6.18 mmol) in Freon-112 (10 ml) was heated at 50-65°C for 19 days. Gas chromatography of the reaction mixture showed presence of nitrile, N-phenyl-perfluoro-n-octylamidine, and imidoylamidine in the ratio 1:1.7:0.2. At that stage, additional nitrile (1.4 g) was added to the reaction mixture and the temperature was increased to 80°C; the reaction was then carried out for a further 21 days. At the end of this period, the ratio of nitrile:triazine:amidine:imidoylamidine was 1:0.3:0.6:0.9, giving the overall yield of the imidoylamidine as 55%. Subsequently, some of the unreacted amidine (0.17 g, 12%) crystallized out of solution and was filtered from the reaction mixture. After evaporation of the solvents, more of the amidine (0.25 g, 17%) was recovered from the residue upon addition of pentane, followed by filtration. The pentane was removed from the filtrate and the rest of the amidine was separated from the solid residue by sublimation. The sublimation residue was washed with pentane and the pale yellow solid which remained (0.31 g, 12% yield) was found to be pure N'-(perfluoro-n-octylimidoyl)-N-phenyl-perfluoro-n-octylamidine, mp 52-53°C. Anal. calcd. for $C_{22}H_7F_{30}N_3$: C, 29.92; H, 0.80; F, 64.53; N, 4.76; MW, 883.27. Found: C, 29.43; H, 0.78; F, 64.50; N, 5.33; MW, 880.

Perfluoro-n-octanonitrile reactions with phenylphosphine

In the sealed tube experiments, the reactants were introduced into the ampoule using a vacuum line assembly. Subsequently, the ampoule was sealed in vacuo and exposed to a selected temperature for a denoted period of time as given in Table 6. After conclusion of heating, the ampoule was opened to the vacuum system and the volatiles were fractionated

from a warming trap through traps held at -23 and -78°C into a liquid nitrogen cooled trap. The separated condensibles, largely phenylphosphine and perfluoro-n-octanonitrile, were then quantitated. The involatile residue was taken up in Freon-113 to remove and quantitate the tetraphenyltetraphosphine; the residue left after solvent removal was analyzed by combined gas chromatography/mass spectrometry (GC/MS). In Test 1, Table 6, $C_7F_{15}C(NH_2)=NCH_2C_7F_{15}$, mp 101-102°C, was isolated by sublimation. Calcd. MW, 794.18. Found, 764 (osmometry).

The experiments where solvent was utilized were performed under nitrogen by-pass. The reaction was monitored by removing aliquots for GC/MS analysis. At the conclusion of the test, the precipitated tetraphenyltetraphosphine was removed and the product mixture, after solvent removal, was subjected to GC/MS analysis. Separations using fractional distillation were unsuccessful in material isolation.

The mass spectral data for all the compounds identified are listed in Tables A-2 through A-5.

Preparation of adduct XXXVI, $C_7F_{15}C(=NH)P(C_6H_5)_2$

A solution of perfluoro-n-octanonitrile (4.02 g, 10.81 mmol) and diphenylphosphine (1.88 g, 10.10 mmol) in 2:3 aceto-nitrile/Freon-113 solvent mixture (24 ml) together with water (0.001 ml) was heated under nitrogen by-pass at 50-53°C for 12 days. Based on GC analysis, the final product ratio was $(C_6H_5)_2PH$: $C_7F_{15}C(=NH)P(C_6H_5)_2$: $(C_6H_5)_2POF$, 1 : 12.4 : 4.3. Distillation of the residue, following solvent removal, gave the pure adduct, $C_7F_{15}C(=NH)P(C_6H_5)_2$ (1.60 g, 27% yield), bp 101-103°C/0.001 mm Hg, mp 61-62°C. Anal. calcd. for $C_{20}H_{11}F_{15}NP$: C, 41.33; H, 1.91; F, 49.03; N, 2.41; P, 5.33; MW, 581.27. Found: C, 41.87; H, 2.12; F, 49.81; N, 2.51; P, 5.76; MW, 570. The mass spectrum is given in Table A-6.

Preparation of the reduced adduct, XXXVII, $C_7F_{15}CH(NH_2)P(C_6H_5)_2$

A solution of perfluoro-n-octanonitrile (10.00 g, 25.31 mmol) and diphenylphosphine (4.67 g, 25.08 mmol) in 50 ml of the 2:3 acetonitrile/Freon-113 solvent mixture was heated under nitrogen by-pass at 50°C for 14 days. On cooling, a white precipitate appeared; filtered in the inert atmosphere (3.10 g, 67%) was found to be pure tetraphenyldiphosphine. The Freon-113 soluble residue (3.61 g, 25% yield), based on GC/MS analysis, consisted essentially of $C_7F_{15}CH(NH_2)P(C_6H_5)_2$. Sublimation at 65-75°C gave pure $C_7F_{15}CH(NH_2)P(C_6H_5)_2$, mp 50-53°C. Anal. calcd. for $C_{20}H_{13}F_{15}NP$: C, 41.18; H, 2.25; F, 48.86; N, 2.40; P, 5.31; MW, 583.28. Found: C, 41.81; H, 2.36; F, 47.96; N, 2.81; P, 5.55; MW, 580. The mass spectrum is given in Table A-6.

Interaction of the adduct XXXVI with diphenylphosphine

A mixture of the adduct, $C_7F_{15}C(=NH)P(C_6H_5)_2$ (100 mg, 0.17 mmol), and diphenylphosphine (30 mg, 0.16 mmol) was heated in a sealed ampoule at 50°C for 4.7 days. Only unchanged adduct was found to be present; no reduction product was detected.

TABLE A-1

Mass spectral breakdown patterns of $R_fC(=NH)NH\phi$ (XIII), $R_fC(=NH)N=CR_f(NH\phi)$ (XV), $R_fC(=N\phi)NH\phi$ (XIV), and $R_fC(=N\phi)N=CR_f(NH\phi)$ (XVI)[a]

m/e	XIII	XV	XIV	XVI
31		4.0		
36		3.8		
39	3.9		3.1	
50	4.9	3.1	3.5	
51	14.4	7.7	14.3	5.1
60	4.8			
64	4.4			
65	7.1	3.1	8.5	
66	3.6			
69	14.5	26.7	12.0	14.5
76	4.0	6.0	5.5	3.5
77	44.2	35.2	85.2	49.5
78	7.5	9.1	9.0	6.2
91	5.4	6.6	3.7	
92	5.6	8.7	25.9	
93	3.5		4.1	
100	3.9	7.1	3.9	3.9
103		8.9	6.6	5.1
104		3.8	3.3	3.7
118	8.0	18.3	4.3	15.5
119	100.0	54.4	6.5	7.2
120	16.5	8.0		
127				3.5
131	6.0	7.5	3.3	4.9
135				3.8
144		4.5		
150	3.4			
153				3.1
167		3.5	4.8	
168	8.3		7.4	
169		8.7		4.0
181		3.1		
194			6.7	
195		7.4	100.0	
196			23.6	
207			4.4	4.5
224			3.0	
243			6.2	
244			3.0	
253			15.1	
254			4.5	

m/e	XIII	XV	XIV	XVI
257		4.0		
271				15.0
272				3.7
295				4.3
331			9.7	
332			3.4	
346			6.6	
452	3.0			
469	13.5	4.3		
470	3.0			
472		10.6	26.5	15.8
473			5.6	3.4
487	14.3	4.2		
488	38.8(M^+)	10.8		
489	8.6			
514		100.0		
515		24.8		
516		3.2		
545			15.6	
546			3.8	
562			4.9	
563			44.3	
564			60.8(M^+)	
565			17.7	
589				4.2
590				100.0
591				36.9
592				6.4
864		25.4		
865		8.6		
881		3.9		
882		3.8		
883		38.2(M^+)		
884		14.3		
940				34.8
941				12.2
958				7.0
959				67.8(M^+)
960				29.8
961				5.9

a) Peaks having intensities lower than 3% of the base peak are not reported; R_f is C_7F_{15}.

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TABLE A-2

Mass spectral breakdown patterns of $R_fCH=NH$ (XVII), $R_fCH_2NH_2$ (XVIII), $R_fCH=NCH_2\dot{R}_f$ (XIX), and $R_fCH_2CH(NH_2)R_f$ (XX)[a]

m/e	XVII	XVIII	XIX	XX	m/e	XVII	XVIII	XIX	XX
27	3.4				131	40.5	11.8	10.8	3.4
28	_100.0_		16.5		133			4.5	
29	9.1	4.6			159	4.7			
30		_100.0_			169	11.3		6.8	
31	8.2	9.9	3.0		181	8.2	3.7		
41			5.4		207	3.1			
43			4.0		281	4.9	4.3		
46	3.2				298		4.8		
50	9.5	3.3			308	5.5			
51	13.0		14.4		328	5.9			
61		28.4			348		18.2		
64			4.9		358	7.3			
69	48.4	19.4	33.2	8.5	360		3.4		
77	5.6				378	44.0			
78	25.9	9.3			379	7.4			
79		24.4			380		55.8		
80		15.0			381		7.8		
81	5.6	4.2			397		4.2		
83			5.4		398	5.0	28.6		
90			16.3		399		3.4 (M+)		
91			7.8		410			_100.0_	8.2
92				5.9	411			14.7	
93	8.3	3.3			412				_100.0_
95			6.1		413				14.2
100	26.6	13.3	6.6		460			4.4	
108	7.5				462				3.5
110		8.4			760			25.5	
112	3.4				761			5.5	
113	7.8				762				24.7
119	19.6	6.3	10.9		763				3.2
122			3.6		780				4.3
128	6.5								

a) Peaks having intensities lower than 3% of the base peak are not reported; R_f is C_7F_{15}.

TABLE A-3

Mass spectral breakdown patterns of $R_fCH_2NHCR_f(=NH)$ (XXIII), $R_fCH_2NHC(R_f)=NCH_2R_f$ (XXVI), $R_fCH_2NHC(R_f)=NCR_f(=NH)$ (XXVII), and $R_fCH=N-C(R_f)=NC(=NH)R_f$ (XXV)[a]

m/e	XXIII	XXVI	XXVII	XXV	m/e	XXIII	XXVI	XXVII	XXV
31	3.1			3.8	476	10.0			
41				3.5	487		5.2		
43	5.0				498				12.0
51		7.3	4.6		499				7.8
53				3.3	500			5.3	
55	9.7	7.9	5.8		501			3.7	
68			4.3		505	10.2			
69	26.3	26.4	25.8	36.7	530				4.6
76				7.9	719		4.0		
77				3.9	755	6.8			
78	3.6		5.9		761			3.9	
79	3.1				773				3.3
83		3.2			774	6.4			
86	4.8				775	38.1		3.8	
90		5.3	3.2		776	9.5			
95		6.0			778		34.9	22.6	
100	7.4	6.1	6.4	7.7	779		8.8	5.6	
105	4.6				780			3.5	
108			3.1	3.1	787		3.1		
110	7.8				794	23.7(M+)			
119	11.1	12.3	10.9	15.5	795	6.5			
126				3.8	797				12.6
131	10.1	9.7	8.1	15.2	798				7.5
156	3.0				799				8.6
169	8.1	13.4	7.2	10.6	800			5.6	
181	3.0		3.0	5.1	801			4.4	
182			4.8		805		3.7		
219		6.2			807		_100.0_		
269		3.7			808		28.4		
360	3.3				809		4.3		
376				3.3	818			20.6	_100.0_
380	5.5				819			7.1	34.3
396	4.3		4.5	4.5	820			_100.0_	6.0
398	3.9		4.0		821			42.3	
405	5.9				822			6.4	
410		7.8			857		42.0		
425	_100.0_				858		12.6		
426	17.4				866				17.8
437		10.3			867				7.8
450			4.4		868				3.7
455	12.6				870			3.0	
458		3.2		3.2	1007		3.4		
475	48.0		3.0						

a) Peaks below m/e 31 and of intensities lower than 3% of the base peak are not reported; R_f is C_7F_{15}.

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TABLE A-4

Mass spectral breakdown patterns of $R_f CH(NH_2)P\Phi H$ (XXVIII), $R_f CH(P\Phi H)N=CHR_f$ (XXIX), and $R_f C(=NH)P\Phi CR_f(=NH)$ (XXXI)[a]

m/e	XXVIII	XXIX	XXXI	m/e	XXVIII	XXIX	XXXI
28	47.1	14.2	9.0	169		9.0	7.8
31	3.2	3.7	3.0	171	3.5	28.6	
39	5.9	3.7		172		4.4	
46			3.1	173		7.0	
50	4.5	5.1	4.1	190		3.1	
51	9.2	10.6	5.1	212			9.1
56	3.4			240		5.9	
57	7.1	5.0		290		3.6	
60	3.3			298	4.9		
65	8.6	7.1		348	28.0		
66	5.9			349	4.0		
69	17.3	43.4	28.0	378	5.5		
75		3.5		379	10.7		
77	7.1	9.6	8.6	390		12.5	
78	11.1	6.4	6.0	398	_100.0_		
79	36.5	3.0		399	17.7		
80	4.3			410		10.0	
81	6.1	4.9	4.0	490		14.9	
83	9.5	10.1		491		6.6	
90		31.7		498		3.5	
96		3.7		501		16.7	
100	7.4	9.2	6.1	502		3.1	
104			3.1	504			3.5
107	18.0	15.8	26.4	507	11.0(M+)		
108	32.4	11.1	_100.0_	508	3.1		
109	27.3	_100.0_	19.8	531			85.4
110	80.1	13.2		532			23.2
111	12.5			568		10.3	
113		4.8		569		3.0	
119	5.9	12.0	12.4	581			4.1
121		5.1		778		51.5	
127	18.0	42.5	39.8	779		15.6	
128	4.7	6.9	5.8	780		3.2	
129	6.5			868		6.3	
131	9.3	13.8	8.5	869		3.4	
135			6.7	870		3.5	
136			6.4	881			29.8
138	3.5			882			9.2
140		5.6		887		24.3(M+)	
143		7.4	5.0	888		6.1	
146		3.1	6.2	900			62.5(M+)
151		3.8		901			19.9
152		3.2		902			3.2
165			7.7				

a) Peaks having intensities lower than 3% of the base peak are not reported; R_f is C_7F_{15}.

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TABLE A-5

Mass spectral breakdown patterns of φ$\overline{PCH(C_7F_{15})NHCH(C_7F_{15})P}$φ (XXXII), φ$\overline{PCH(C_7F_{15})NHCH(CFHC_6F_{13})P}$φ (XXXIII), and $C_7F_{15}CH(PφH)N=CHCFHC_6F_{13}$ (XXXIV)[a]

m/e	XXXII	XXXIII	XXXIV	m/e	XXXII	XXXIII	XXIV	m/e	XXXII	XXXIII	XXXIV
28	24.2	18.7	13.0	151	8.3	7.1	3.3	490	3.1		4.0
31	5.6	5.4	5.8	152	6.5	5.5	3.1	491		.	8.1
39			4.8	153	3.1	10.2	9.5	492			5.9
50	5.6	3.7	4.9	154	3.3	7.9		497	5.9		
51	12.3	9.7	9.3	157	3.9	4.2		504	3.4		
57	4.6	3.2	6.9	164		3.0		505	4.7		
65			9.8	165	4.4	5.1		550			9.8
69	28.0	21.5	22.6	169	4.6	3.1	3.7	580		17.8	
72		8.6	23.3	171	22.7	13.0	16.2	581		6.8	
75	4.0	4.4		172	10.7	4.4	4.9	598	17.7	17.4	
76		3.1		173			8.1	599	6.3	5.7	
77	24.0	17.0	5.9	181	3.0	3.8		608		18.3	
78	6.7	5.8	6.0	182	3.2	3.6		609		4.8	
79	3.3			183	34.6	25.1		626	35.1	12.0	
81	5.7	4.1	4.6	184	7.6	7.8		627	12.1	3.9	
83	3.2		9.9	185	100.0	81.9		710			4.1
90	14.6	8.7	18.3	186	23.3	22.1		722			13.6
95		4.3	3.6	187		3.2		723			4.1
96			3.8	214	3.2			742		5.7	3.5
100	6.2	5.7	6.0	216	24.1	11.3		760	9.7	7.5	100.0
102	4.3	3.2		217	49.1	39.4		761			30.7
107	23.8	19.7	15.3	218	10.1	9.6		762			4.2
108	22.8	19.1	17.1	222			6.4	829			3.0
109	17.3	15.7	56.6	229	19.3	17.3		831			5.5
110	3.2		13.7	230	4.0	3.4		850			13.1
113	4.1	3.4	4.4	235		3.7		851			3.8
119	8.4	6.4	7.5	240			4.1	868		3.7	
121	5.7	3.0	5.0	372		4.3	7.3	869		4.2	56.9(M+)
122			4.3	390	10.2	3.9	7.2	870			17.8
123		18.6		392		3.6	3.6	871			3.0
127	42.7	39.5	36.2	410	10.1	4.2		917	3.5		
128	6.6	6.4	8.2	442		22.8		958		24.1	
131	8.1	5.9	6.1	443		3.0		959		11.8	
133	4.1	5.3		460	26.9			976	27.0	8.0	
134		3.4	3.7	461	5.6			977	9.3	100.0(M+)	
136	3.5			468			4.8	978		36.7	
138	22.2	15.1		472		5.3	11.1	979		8.5	
139	48.1	39.9		486	5.8	3.7		995	98.2(M+)	5.1	
140	7.9	8.7	7.4	487		6.3		996	35.3		
141	23.3	3.1	3.3	488		7.3		997	8.9		
146		3.5	3.2								

a) Peaks having intensities lower than 3% of the base peak are not reported.

TABLE A-6

Mass spectral breakdown patterns of $C_7F_{15}C(=NH)P(C_6H_5)_2$, XXXV, and $C_7F_{15}CH(NH_2)P(C_6H_5)_2$, XXXVI [a]

m/e	XXXV	XXXVI	m/e	XXXV	XXXVI	m/e	XXXV	XXXVI
31	5.9	7.3	110		9.1	197		3.6
39	8.2	8.9	113		3.4	202		3.1
48		3.6	115	7.7	8.3	203	3.5	5.4
50	7.9	8.8	119	15.8	8.9	204	4.3	6.4
51	15.8	20.0	120	3.0	3.4	211	9.4	
52	3.4	3.9	126	3.9	3.4	212	40.1	
56	3.6	4.4	127	17.8	12.5	213	14.3	
57	9.7	11.4	128	5.6	6.9	214		3.6
62		3.9	129		5.8	219	3.5	
63	5.8	23.0	131	13.5	14.6	262	7.6	
65	5.0	7.1	133	7.7	9.0	293		5.1
66		5.6	135	4.0	5.0	294		4.9
69	27.7	20.1	138	3.5		298		5.1
75	3.1	3.8	139	4.5	5.0	348		19.2
76	8.6	3.4	140		3.0	371		10.5
77	15.3	10.7	141	6.2	7.0	372		4.1
78	7.9	16.1	151	3.1	3.9	378		10.1
79	3.8	31.6	152	16.6	19.8	396	4.5	
80	4.0	6.2	153	5.2	6.1	398		27.9
81	9.8	10.6	154	4.4	6.5	399		5.6
82	4.3	5.6	157	7.6	8.9	416	6.7	
83	5.1	7.6	159	3.1	4.5	472	3.4	
89		3.0	169	14.2	4.8	503	3.9	
91	5.7	5.6	170	8.8	9.5	544		5.4
92	13.0	8.4	171		3.4	562	12.8	
93	6.6	7.5	177	3.6		563	4.1	
96		3.2	181	20.5	13.4	564		18.6
100	10.4	10.4	182	12.8	13.0	565		4.7
102		3.4	183	56.1	60.4	567		3.1
104		3.4	184	22.4	24.8	581	$100.0(M^+)$	
106	4.2	8.8	185	66.0	50.7	582	26.2	
107	26.5	38.1	186	35.5	100.0	583	8.0	$13.7(M^+)$
108	39.3	76.3	187	8.2	54.3	584		8.7
109	15.6	25.9	188		10.0			

a) Peaks having intensities lower than 3% of the base peak are not reported.

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